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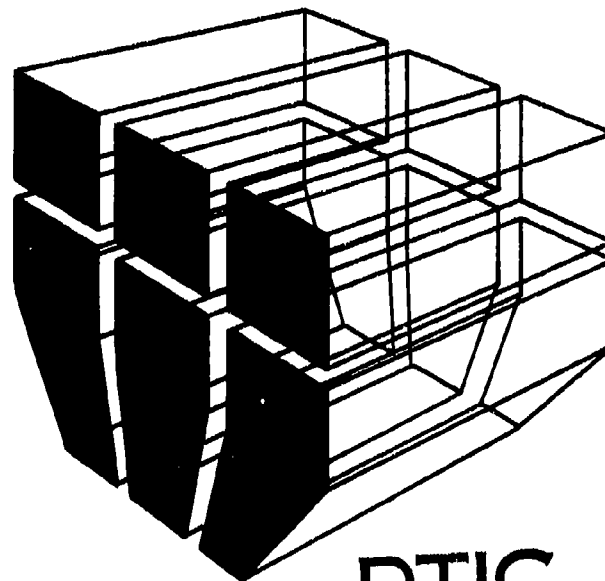
STRATEGIES FOR CONTROLLING AND REMOVING TRACE ORGANIC COMPOUNDS FOUND IN POTABLE WATER SUPPLIES AT FIXED ARMY INSTALLATIONS

by

L. E. Lang
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This report documents research to inform fixed Army installations about: (1) the type and characteristics of trace organic compounds that may be found in drinking water, (2) existing and proposed drinking water standards for trace organic compounds, (3) analytical techniques for measuring organic contaminants in water, and (4) treatment processes and/or operational modifications for formulating a cost-effective strategy to control or remove organic contaminants from potable water.

The sources, types, characteristics, and significance of organic compounds likely to be found in drinking water were reviewed. Current and proposed standards for organic compounds in drinking water and compounds being considered for regulation were studied, as were analytical techniques to isolate, resolve and identify, and quantify these compounds. Operational modifications for controlling the formation of organics, particularly trihalomethanes, also were reviewed. Treatment techniques for removing synthetic trace organic compounds were identified. Case studies, cost data, and design guidance were consulted to help select a cost-effective way to provide safe potable water on fixed Army installations.



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To provide this information, the sources, types, characteristics, and significance of organic compounds likely to be found in drinking water were reviewed. In addition, current and proposed standards for organic compounds in drinking water as well as compounds being considered for regulation were studied, as were analytical techniques used to isolate, resolve and identify, and quantify these compounds.

Operational modifications for controlling the formation of organics, particularly trihalomethanes, also were reviewed. Treatment techniques for removing synthetic trace organic compounds were identified, with proven technologies emphasized. Case studies, cost data, and design guidance were consulted to aid in selecting an appropriate, cost-effective strategy for providing safe potable water on fixed Army installations.

FOREWORD

This research was conducted for the Directorate of Engineering and Construction, Office of the Chief of Engineers (OCE) under Intra Army Order E87840048 dated 23 February 1984 from the U.S. Army Engineer Division, Huntsville. The work was performed by the Environmental Division (EN), U.S. Army Construction Engineering Research Laboratory (USA-CERL) in conjunction with the University of Texas at El Paso, DACW 88-84-D-0005 under EN 4-260. S. P. Shelton was an employee of the University of Texas. The OCE Technical Monitor was W. Medding, DAEN-ECE-G. Dr. R. K. Jain is Chief, EN.

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STRATEGIES FOR CONTROLLING AND REMOVING TRACE ORGANIC COMPOUNDS FOUND IN POTABLE WATER SUPPLIES AT FIXED ARMY INSTALLATIONS

1 INTRODUCTION

Background

Concern is growing over the literally hundreds of organic compounds discovered in drinking water. Based on Federal and state surveys to date, over 700 organic compounds have been identified in drinking water supplies on Army installations as well as in the general public.¹ Many are toxic and suspected carcinogens, even in minute concentrations. These compounds may be present in potable water as a result of chlorine reacting with naturally occurring organic acids or in surface and groundwater supplies contaminated with pesticides, solvents, or petroleum product constituents.

The widespread use of a broad array of organic compounds such as pesticides, solvents, and petroleum products has increased the potential for water supply contamination by runoff, spills, improper disposal practices, or use in water storage vessels or pipelines. Volatile organic compounds have been detected at the alarmingly high level of several thousand micrograms per liter in both civilian² and Army water supplies.³ Trichloroethylene (TCE), a common solvent used at Army installations and in the civilian sector, is the synthetic organic compound found most frequently in Federal and state groundwater surveys. The U.S. Environmental Protection Agency (USEPA)-recommended standard for TCE concentration in potable water is zero.

Federal and state regulations have now been established limiting these compounds' presence in drinking water. So far, seven organic compounds are regulated and standards are proposed for others. Several more are being considered for regulation. These regulations have caused thousands of public and private wells to be closed. Water treatment plants have had to be upgraded to enable organics removal and equipment has had to be installed to treat water supplies not served by a treatment plant. This trend to regulate levels of organic compounds in drinking water is likely to continue as the compounds' health effects become known and the ability to detect them becomes more refined.

Army installations must comply with the regulations limiting organic compounds in drinking water. In some cases, this may involve installing additional treatment facilities. A recent survey⁴ of water treatment facilities at Army installations revealed that 41 percent of the installations surveyed are supplied by groundwater. These installations are the ones most likely to have a water supply contaminated by chlorinated

¹J. E. Dyksen and A. F. Hess III, "Alternatives for Controlling Organics in Groundwater Supplies," *Journal of the American Water Works Association (JAWWA)*, Vol 74, No. 8 (August 1982).

²J. E. Dyksen and A. F. Hess III.

³U.S. Army Environmental Hygiene Agency (AEHA), *Water Quality Information Paper No. 35* (February 1982).

⁴L. E. Lang, J. T. Bandy, and E. D. Smith, *Evaluating and Improving Water Treatment Plant Processes at Fixed Army Installations*, Technical Report N-85/10 (U.S. Army Construction Engineering Research Laboratory [USA-CERL], 1985).

hydrocarbon solvents, which are not removed effectively by conventional treatment. Furthermore, installations served by groundwater supplies often have no treatment facilities beyond chlorination and fluoridation. Of 44 installations surveyed, over half have conventional water treatment facilities, but these processes remove only certain types of organic compounds. The pervasiveness of organic compounds in the environment means that all Army installations are susceptible to water supply contamination and would be required to install removal equipment or to modify existing operations if these compounds are detected.

Information is needed to help installations understand the types, characteristics, and significance of organic contaminants causing concern and to identify which compounds are regulated. Guidance also is needed in designing and selecting treatment methods and operational modifications to control or remove trace organic compounds. This would help in developing an appropriate, cost-effective strategy for providing safe potable water to Army installations.

Objective

The objective of this work is to provide fixed Army installations with information on: (1) the sources, types, characteristics, and significance of trace organic compounds that may be found in drinking water, (2) existing and proposed drinking water standards for trace organics as mandated by the Safe Drinking Water Act, (3) analytical techniques for measuring trace organic contaminants in water, and (4) treatment processes and operational modifications that can be used to formulate a cost-effective strategy for controlling or removing organic contaminants from potable water.

Approach

The literature was reviewed, including documents covering regulations. Applicable information was organized into four chapters giving (1) background on the contaminants of concern, (2) overview of analytical techniques used, (3) treatment plant designs, and (4) operational techniques for controlling trace organic contaminants in water supplies. Knowledge of the status of Army water treatment facilities as well as lessons learned about organic contaminant removal in the private sector also were investigated and incorporated.

Scope

This report aimed toward fixed Army installations that must monitor and remove organic contaminants found in drinking water, particularly compounds regulated by standards or proposed for regulation. The treatment processes described can remove a wide variety of organic compounds, including those now regulated and others with potential for reaching Army installation water supplies.

Mode of Technology Transfer

This work is the basis for an Engineer Technical Letter. Information presented here also may apply to the following Technical Manuals: TM 5-660, *Operation of Water Supply and Treatment Facilities at Fixed Army Installations*, and TM 5-813-3, *Water Supply: Water Treatment*.

2 CONTAMINANTS OF CONCERN

History

The driving force for controlling organic compounds in drinking water has been the Safe Drinking Water Act, which was passed in 1974, and the subsequent detection of so many potentially dangerous organic compounds in drinking water supplies. The first set of regulations--the National Interim Primary Drinking Water Standards--became effective in 1977 and established enforceable limits on the concentration of trihalomethanes (THMs) and six pesticides in potable water.

In the past 12 years, Federal and state surveys have identified additional organic compounds in water supplies. Based on these findings, the USEPA in 1984 proposed standards for nine synthetic volatile organic compounds (VOCs). These standards would be based on the compounds' frequency and level of occurrence and potential health effects as well as the analytical methods available to detect the compound in the water supply. Several other synthetic organic compounds are being considered for regulation, pending tests for carcinogenicity and health risk assessment.

Organic Compounds With Standards or Proposed Standards

Contaminants that now have enforceable standards or Maximum Contaminant Levels (MCLs) under the Interim Primary Drinking Water Standards are total THMs (total content) and six pesticides. THMs are discussed in a separate section of this chapter and the six pesticides are listed in Table 1. Four pesticides are chlorinated hydrocarbons and two are chlorophenoxys. These compounds do not occur naturally and have been used to control vegetation, fish, and aquatic insects. They can reach the water supply from (1) runoff, (2) spills or leaks from storage vessels, or (3) wastewater discharged during the compounds' manufacture or use. Two pesticides, Lindane and 2,4-D, are used commonly at Army installations.

Table 2 lists the nine synthetic VOCs for which USEPA has proposed standards. At this time, the standards are Recommended Maximum Contaminant Levels (RMCLs), which means they are nonenforceable health goals. During the next 2 years, USEPA will propose enforceable MCLs for these contaminants. The MCLs are to be close in value to the RMCLs and based on health, treatment technology, costs, and other considerations.⁵ Adverse health effects associated with these contaminants include mutagenic and carcinogenic potential, nervous system damage, cardiotoxicity, and liver and kidney damage.

The VOCs in Table 2 are almost all chlorinated hydrocarbons; they are volatile and not very soluble in water. Trichloroethylene (TCE) and tetrachloroethylene (PCE) have been found most frequently in the groundwater supplies surveyed.⁶ Chlorinated hydrocarbons are used commonly as solvents and have a wide array of other uses, such as in manufacturing coatings, inks, oils, plastics, and other chemicals, fumigants, and refrigerants. Benzene, an aromatic hydrocarbon, is used in many products such as resins, detergents, pesticides, fuels, and synthetic materials. These contaminants all can reach water supplies after leaking from storage containers, leaching from paints and other

⁵ Federal Register, Vol 49, No. 114 (12 June 1984).

⁶ J. E. Dyksen and A. F. Hess III.

Table 1**Organic Compounds Regulated Under Interim
Primary Drinking Water Standards (MCLs*)**

Compound	MCL (mg/L)
Total THM	0.1
Endrin	0.0002
Lindane	0.004
Toxaphene	0.005
2,4-D	0.1
2,4,4-TP (Silvex)	0.01
Methoxychlor	0.1

*Maximum Contaminant Levels.

Table 2**Proposed Standards (RMCLs*) for Volatile
Synthetic Organic Compounds**

Compound	RMCL (mg/L)
Trichloroethylene (TCE)	0
Tetrachloroethylene (PCE)	0
Carbon tetrachloride	0
1,1,1-Trichloroethane	0.2
Vinyl chloride	0
1,2-Dichloroethane	0
Benzene	0
1,1-Dichloroethylene	0
Dichlorobenzene	0.75

*Recommended Maximum Contaminant Levels.

coatings, or being used in pesticides, fungicides, herbicides, and at manufacturing plants. Many have been designated "hazardous substances" under regulations resulting from the Federal Water Pollution Control Act (40 CFR 116), are regulated as Hazardous Wastes under regulations pursuant to the Resource Conservation and Recovery Act (40 CFR 261 Subpart D), or are listed as Priority Pollutants in USEPA's National Pollutant Discharge Elimination System. The compounds are used at Army installations as solvents (e.g., TCE) or as constituents of petroleum products (e.g., benzene).

Organic Compounds Being Considered for Regulation

Synthetic organic compounds being considered for regulation include several registered pesticides, some polynuclear aromatic hydrocarbons (PAHs), certain esters, and acrylamide (Table 3).⁷ Which of these will be regulated depends on results of carcinogenicity tests and other health risk assessments. The pesticides being considered have been detected in drinking water supplies, are registered for use in or around drinking water, or potentially could reach water supplies. The PAHs can enter drinking water supplies when coal tar products leach from tank coatings and pipe linings. The phthalates (phthalic acid) and adipates (adipic acid), used in manufacturing, are insoluble in water and do not degrade easily. Acrylamide is used in water treatment processes and may be toxic to the nervous system; it also may be carcinogenic.

The great number of organic compounds in use presents significant potential for contamination of water supplies by several processes, such as leakage and spills from storage and transport vessels, inappropriate disposal practices, and leaching action from organic compounds exposed or applied to the environment.

Trihalomethanes (THMs)

The THMs found in drinking water supplies usually are formed upon chlorination of precursor organics in the raw water supply. As the name implies, these compounds are derivations of methane. THMs are formed when one, two, or three of methane's (CH_4) four hydrogen atoms are replaced by a halogen. Chlorine, bromine, or iodine atoms are actually the only halogens of concern. Ten molecular combinations are possible in THM formation, as Figure 1 shows.⁸ In surface waters, chloroform and bromodichloromethane are the primary THMs because of the humic precursors' characteristics. In groundwater systems, the species formed are more difficult to predict since the precursor source in groundwater can vary widely. The general chlorine/organic precursor reaction that generates THMs can be expressed as:



Chlorine is a very effective disinfectant for potable water treatment and distribution systems. This benefit outweighs the risk of THMs' suspected carcinogenic effects; however, methods for controlling THMs without compromising the bacterial quality of potable water should be pursued with vigor.

⁷ Federal Register, Vol 48, No. 194 (5 October 1983).

⁸ K. W. Timmerman, *An Investigation and Evaluation of Trihalomethanes in Public Drinking Water on Hilton Head Island, South Carolina*, Unpublished Masters Thesis, University of South Carolina, Columbia (1983).

Table 3

Organic Compounds Being Considered for Regulation*

Aldicarb	Dibromochloropropane
Chlordane	1,2-Dichloropropane
Dalapon	Pentachlorophenol
Diquat	Picloram
Endothall	Dinoseb
Glyphosate	Alachlor
Carbofuran	Ethylene dibromide
1,1,2-Trichloroethane	Epichlorohydrin
Vydate	Dibromomethane
Simazine	Toluene
PAHs	Xylene
Atrazine	Adipates
Phthalates	Hexachlorocyclopentadiene
Acrylamide	2,3,7,8-TCDD (Dioxin)

*From: *Federal Register*, Vol 48, No. 194 (5 October 1983).

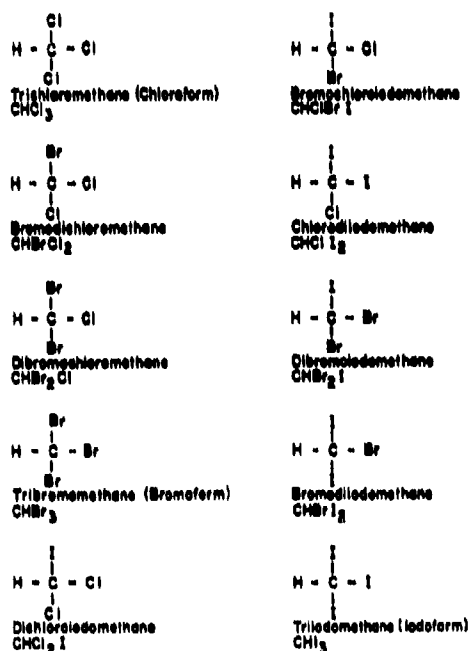


Figure 1. Structural formulas and names of the trihalomethanes. (From: K. W. Timmerman, *An Investigation and Evaluation of Trihalomethanes in Public Drinking Water on Hilton Head Island, SC*, Unpublished Masters Thesis, University of South Carolina, Columbia [1983].)

THM precursors are products of naturally occurring humic and fulvic acids or other organics from industrial discharges that find their way into the raw source water. Although the surface water route is the most common, groundwater supplies often are contaminated by return flows from industrial sources (e.g., spills, leaking tanks) and natural sources (e.g., swamps, bogs).

Besides the presence of precursors and chlorine, several other components are critical in THM formation. Specifically, water temperature, pH, bromine concentration, and chlorine contact time contribute greatly to the rate of THM formation. For example, Ohio River water was evaluated for chloroform formation as a function of temperature and pH.⁹ The temperature range evaluated was between 3 and 40°C. Figure 2 presents data that were collected at three times during a 1-year period. The coincident variation of chloroform in the Cincinnati water distribution system ranged between 30 and 200 µg/L. Water temperature variations were identified as one component of the chloroform variation due to the impact of temperature on reaction rates. Other factors may also affect the variation such as the fluctuation in humics due to the season of the year.

It has also been reported that pH affects the reaction rate in THM formation.¹⁰ The formation rate tends to increase with increasing pH, as Figure 3 shows. However, the ultimate amount of THM formed appears to be relatively independent of pH; only the rate of reaction is pH-dependent.

Bromine also has been shown to affect the rate and character of THM formation.¹¹ Specifically, as the bromine concentration increases, the rate of chloroform formation decreases while that of bromoform formation increases. The mixture of brominated forms will dominate the chlorinated forms and the total THM concentration may increase relative to the same water without bromine.

This particular phenomenon may have major impact on Army installations located in coastal or desert regions. In coastal areas, one of the most common groundwater problems is saltwater intrusion, whereas in deserts groundwater mining results in saline water rising up from lower aquifers. Incident to saltwater intrusion is intrusion by the bromine contained in most saltwater systems (both seawater and saline inland aquifer). If a saltwater-contaminated aquifer is used as a potable water source, brominated THMs will form when enough organic precursors are present.

⁹M. D. Arguello, et al., "Trihalomethanes in Water: A Report on the Occurrence, Seasonal Variation in Concentrations, and Precursors of Trihalomethanes," JAWWA, Vol 71, No. 9 (September 1979); J. M. Symons and G. G. Robeck, "Treatment Processes for Coping With Variation in Raw Water Quality," JAWWA, Vol 67, No. 3 (March 1975); J. M. Symons, et al., "National Organics," JAWWA, Vol 67, No. 11 (November 1975).

¹⁰M. D. Arguello, et al.; American Water Works Association (AWWA), *Analyzing Organics in Drinking Water*, AWWA Technical Resource Book (1981).

¹¹AWWA, "Organic Contaminants in Water," Committee Report, JAWWA, Vol 66, No. 11 (November 1974); AWWA, 1981.

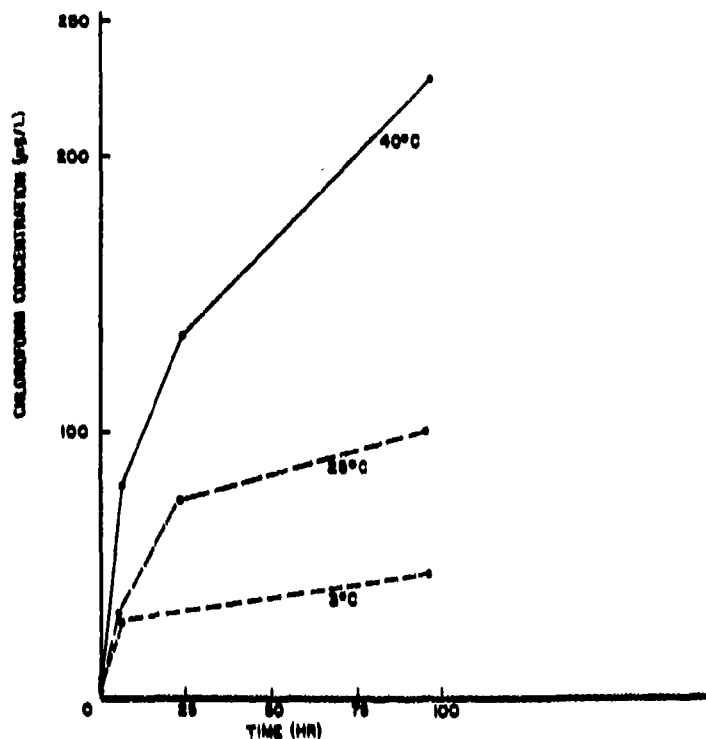


Figure 2. Chloroform formation at varying temperatures.

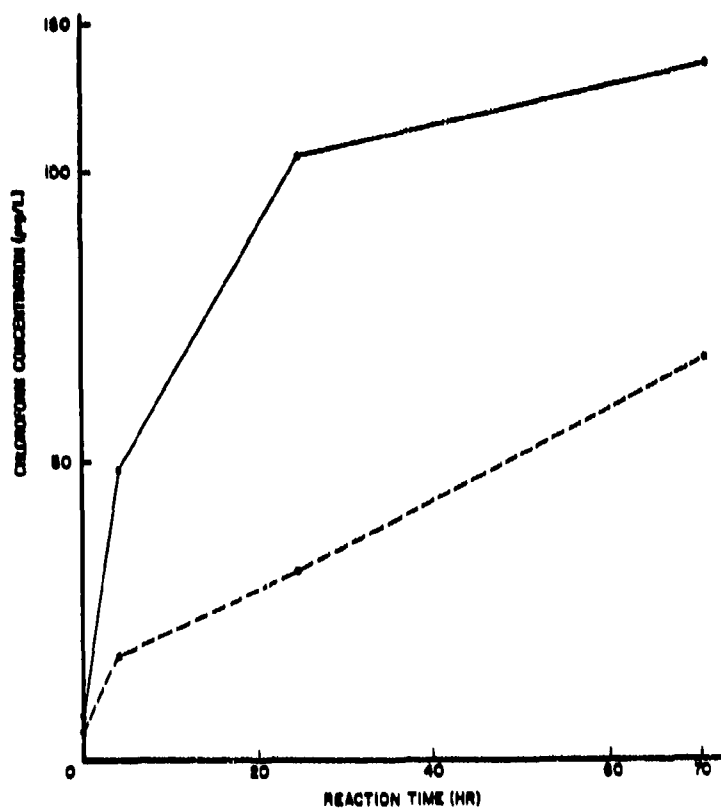


Figure 3. Effect of pH on chloroform production.

The final major factor affecting THM formation is chlorine contact time.¹² The reaction rate depends on the precursors, environment, and chlorine species available; therefore, sampling strategies must consider the contact time between chlorine addition and measurement of THM concentrations to insure comparability of laboratory data. Reaction rate curves often can be developed for a given water, environment, and chlorine combination.

THMs are considered the most prevalent organic problem in potable water supplies. They can be generated in several ways and can change character for many very subtle reasons. Methods for control and treatment are discussed in Chapter 4 in the sections entitled Oxidation/Disinfection—THM Control, Chemical Coagulation, Evaluating How to Improve Coagulation, and Activated Carbon Adsorption, and in Chapter 5 in the section Air-Stripping. Additional information is in USA-CERL Technical Report N-85/10.

¹²D. J. Moore, *Trihalomethanes in Drinking Water: Four Unit Processes for Removal*, Report USC-CE-79-104, University of South Carolina, Columbia (August 1979); J. J. Richard and G. A. Junk, "Liquid Extraction for the Rapid Determination of Halomethanes in Water," *JAWWA*, Vol 69, No. 1 (January 1977).

3 ANALYSIS OF TRACE ORGANICS IN WATER

One criterion the USEPA used in selecting VOCs to be regulated is the availability of analytical methods to detect the contaminant. For this reason, a discussion of methods for determining the concentration of organic contaminants is merited.

Analyzing trace organics in water involves determining the amount and type of carbon-containing molecules present. To achieve this objective, numerous methods have been developed for isolating, resolving, identifying, and quantifying (detecting) the complex mixtures of organic compounds present in water. Figure 4 illustrates the methods involved in the isolation, resolution, and detection steps. Organic compounds in water typically are delineated on the basis of polarity, volatility, and molecular weight. With this in mind, the methods for trace organic analysis can be categorized into a uniform conceptual approach.¹³

Trace organic analysis has advanced greatly over the past decade; however, much more progress must be made before all organics in water can be identified.¹⁴ Of the 2 million organic compounds known, only 500, or 0.03 percent, have been detected in water supplies. Current detection limits at the microgram per liter level, but it is anticipated that increased numbers of compounds will be found as detection limits reach the nanogram or picogram level. This increase is predicted based on the trend observed from historical detection levels of 1 mg/L, when approximately 50 organics were known to contaminate water supplies, to present technology. If progress continues at the same rate (one order of magnitude of new organics per three-order magnitude of detection), by the time picogram detection limits are reached, some 5 million organic chemicals could be detected, assuming that many existed.

Even though very few of the organics in water supplies have been identified,¹⁵ considerable information is available characterizing many compounds. This information is useful in classifying organics for both analysis and unit process design.

The criteria defined previously for classification are volatility, molecular weight, and polarity. "Volatility" is the physical property of vaporizing or evaporating quickly and corresponds roughly with the boiling point of the compound. Volatility has applications in analytical concentrating techniques and in treatment strategies such as air-stripping. "Molecular weight" is the number of grams in 1 mole of a substance. This characteristic can be used in analytical separation procedures and in treatment for selective adsorption properties. The final classification component, "polarity," describes the degree to which one part of a molecule is more positively or negatively charged than the other. Polarity helps determine how effective adsorption is at removing organic compounds.

¹³ I. H. Suffet and J. V. Radzyl, "Guidelines for the Quantitative and Qualitative Screening of Organic Pollutants in Water Supplies," JAWWA, Vol 68, No. 10 (October 1976).

¹⁴ AWWA, 1981; R. C. Dressman, et al., "Comparison of Methods for Determination of Trihalomethanes in Drinking Water," JAWWA, Vol 71, No. 7 (July 1979).

¹⁵ R. C. Dressman, et al.; AWWA, 1981.

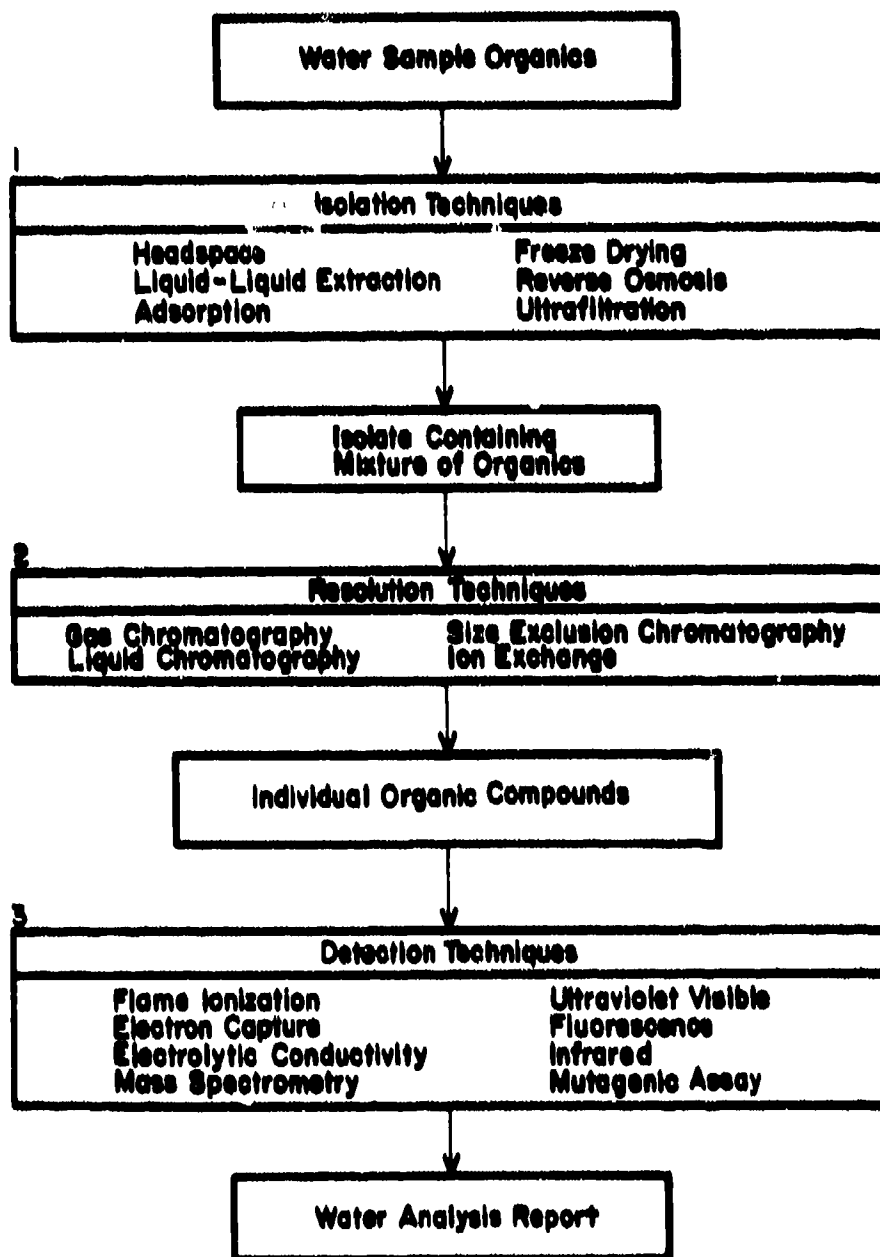


Figure 4. Steps in analyzing organics in water. (From: R.R. Trussell and A. R. Trussell, "Evaluation and Treatment of Synthetic Organics in Drinking Water Supplies," JAWWA, Vol 72, No. 8 [AWWA, August 1980]. Used with permission.)

Table 4 lists some organics that have been found in water supplies, classified according to volatility, molecular weight, and polarity.¹⁶ The schematic is a generalization with many overlapping areas, omissions, and exceptions to the classifications shown. Variations also are possible within each chemical class, for example, substitution by a halogen. Even with these limitations, the trends shown are valid for the number of organic compound classes.

Table 5 gives methods for isolating organics using the same framework as Table 4. The most volatile, polar, and water-soluble organics generally are not isolated but are directly subjected to analysis, such as direct injection gas chromatography.¹⁷ Less polar volatile organics are isolated by allowing them to partition into the gaseous phase (headspace) above the water; partitioning can be enhanced by using dynamic gas flow or by trapping the organics after they enter the gas phase. More polar organics, which are difficult to recover with the dynamic headspace/adsorption technique, can sometimes be isolated through a concentrating distillation step before headspace removal.¹⁸

Liquid-liquid extraction (LLE) techniques, in which organics are partitioned into an organic solvent brought into contact with the water sample, can be used with semivolatile compounds. LLE methods typically are not applied to volatile compounds because extraction is followed by boiling-off the solvent for concentration. However, the LLE technique without the concentration step has been used widely for THM analysis. For more polar organics that are less amenable to LLE, a pH adjustment or derivatization often converts them to an extractable form.

When isolating organics from large amounts of water, the adsorption/elution method can be used.¹⁹ "Adsorption" is a material property in which molecules adhere to a surface with which they come into contact due to forces of attraction on the surface.²⁰ In this technique, organics are trapped on an adsorbent resin or activated carbon and subsequently desorbed by washing with an organic solvent. Selected resins that cover a wide range of polarities can be used to maximize recovery of various organics of concern in the same way that solvent polarity can be varied in LLE techniques. Adsorption/elution often is more suitable than LLE for high molecular weight organic compounds because these compounds' kinetics of adsorption are faster than their partitioning equilibrium.

The most polar-heavy organics are best suited to vacuum distillation and freeze-drying techniques, which remove water selectively and leave the organic behind as a residue. Less polar, high molecular weight organics are isolated by reverse osmosis and ultrafiltration. Reverse osmosis uses a pressure-induced gradient to concentrate organics and other specified solutes on a membrane's low pressure side. Ultrafiltration is a similar process but concentrates solutes by molecular weight rather than chemical nature.

¹⁶AWWA Committee Report, 1974; AWWA Committee Report, "Organic Contaminants in Water Supplies," JAWWA, Vol 67, No. 8 (August 1975); C. M. Bolton, "Cincinnati Research in Organics," JAWWA, Vol 67, No. 7 (July 1975).

¹⁷AWWA, 1981.

¹⁸J. P. Mieure, "A Rapid and Sensitive Method for Determining Volatile Organohalides in Water," JAWWA, Vol 69, No. 1 (January 1977).

¹⁹A. R. Trussell, et al., "Precise Analysis of Trihalomethanes," JAWWA, Vol 71, No. 7 (July 1979).

²⁰W. Weber, *Physicochemical Processes for Water Quality Control* (Wiley Interscience, 1971).

Table 4

Schematic Classification of Organics Found in Water

Polarity	Volatility							
	Volatile				Semivolatile		Nonvolatile	
Polar	Alcohols Ketones Carboxylic acids				Alcohols Ketones Carboxylic acids		Polyelectrolytes Carbohydrates Fulvic acids	
Semipolar	Ethers Esters Aldehydes				Ethers Esters Aldehydes Heterocycles		Proteins Carbohydrates Humic acids	
Nonpolar	Aliphatic, aromatic hydrocarbons				Aliphatic, aromatic, alicyclic, aromatic hydrocarbons		Lignin	
Molecular Weight	Low				Medium		High	

Table 5

Isolation of Organic Compounds Found in Water

Polarity	Volatility							
	Volatile				Semivolatile		Nonvolatile	
Polar	None				Derivatization			
	Distillation				Liquid-liquid extraction pH Adjustment		Adsorption Elution Vacuum distillation Freeze drying	
Semipolar	Headspace				Liquid-liquid extraction		Reverse osmosis	
	Dynamic headspace adsorption				Adsorption Elution			
Nonpolar	Headspace adsorption				Liquid-liquid extraction		Adsorption Elution	
	Headspace						Ultrafiltration	
Molecular Weight	Low				Medium		High	

Some factors that influence isolation of organics from water are temperature, pressure, equilibration time, ionic strength, pH, and particulate adsorption. With the exception of particulate adsorption, these factors typically can be standardized for a specific application to maximize recovery. Natural waters vary greatly in particulate characteristics; thus, the surface properties of the particulates, which can absorb and desorb organics, may vary widely among waters evaluated. Particulates pose the most difficult issue in current isolation techniques relative to reproducibility of results.

After the organic(s) of concern have been removed from the water, the isolate typically contains a complex mixture of organic compounds. The most common technique used to resolve this mixture is chromatography, a process of selectively separating the components of a mixture into distinct constituents. Chromatography is a complex phenomenon, combining aspects of thermodynamics, kinetics, and transport properties.

Chromatographic separation usually is achieved by one of four techniques: adsorption, partitioning, size exclusion, and ion exchange. In adsorption chromatography, the organic mixture is transported in a mobile fluid phase across a solid stationary phase. As the organics travel across the stationary phase, each compound spends a characteristic amount of time bound statically to the solid phase. Thus, the compounds elute one at a time from the end of the solid phase with the least adsorbed organic evolving first. Adsorption chromatography is best suited for resolving organics with polar groups that promote selective adsorption.

Partition chromatography is similar, but the solid phase is coated with a stationary fluid into which organics dissolve rather than adsorb. Therefore, partitional systems can be used for both polar and nonpolar organics.

Size-exclusion chromatography (SEC) separates organics according to molecular weight through a permeation or filtration process.²¹ In the permeation process, organics travel through a medium containing many small pores. The smaller compounds spend a high percentage of time in the pores whereas the larger compounds spend much less time in the pores. Therefore, organic compounds are eluted selectively from the column with the high molecular weight fraction coming off first. In the filtration mode of SEC, the elution order is reversed.

Ion-exchange chromatography involves the interchange of ions in the mixture to be resolved with ionic groups on a synthetic organic resin. Compounds least favorably held by the resin come off the column first. Since ion exchange is an electrostatic attraction process, the organics suitable for this process are those containing or transformed to compounds containing ionic functional groups.

Table 8 summarizes resolution techniques for the different classes of organic compounds found in water. Although a theoretically sound resolution technique is available for each type organic compound present in water, the technology for using gas as the mobile fluid phase is developed better than liquid-carrier techniques. Before the 1970s, gas chromatography dominated the other procedures because of superior speed, resolution, and detectors. However, recent improvements in high-pressure liquid systems have greatly increased the use of high-resolution liquid column chromatography. This

²¹ AWWA, 1981.

procedure separates liquid-soluble organics, in addition to gas-soluble or volatile compounds, by high-pressure liquid chromatography.

Once organics in water have been isolated and separated, they must be identified and quantified. Table 7 lists detection devices typically used for observing the organics' physical and chemical properties. Although many organics have characteristics well suited to detection by several techniques, the best detectors for both volatile and semivolatile organics are those used in conjunction with gas chromatography.

The flame-ionization detector is a relatively sensitive, nonspecific, universal device for detecting organic compounds with a wide dynamic range. The electron capture detector is very sensitive and is specific for compounds containing oxygen, halogens, nitrogen, and several other organics. The thermionic or alkali flame detector also is highly sensitive and has two variations: one that detects organics containing phosphorus, the other for nitrogen-containing organics. Electrolytic conductivity and microcoulometric detectors are moderately sensitive and are specific for compounds containing halogen, sulfur, and nitrogen. All of these detectors have linear ranges greater than 1000 and therefore can both identify and quantify organic compounds. The mass spectrometer is one of the most useful detectors because it reveals specific information about the structures of organics being analyzed. Thus, unknown compounds can be identified and then quantified using one of the more linear detectors.

The nonvolatile, high molecular weight organics are more difficult to detect and quantify. Because these molecules are so large and typically contain several organic groups, the physical/chemical properties are manifested as a composite. These properties can be observed using several different detectors: ultraviolet-visible absorbance, fluorescence, infrared absorbance, nuclear magnetic resonance, and photoconductivity. Bioassay techniques sometimes are used for organic species detection. Mutant isolates of an organic often can identify and sometimes quantify carcinogenic potential.

Another approach used for isolating nonvolatile, nonpolar, heavy organics is division of the molecules into identifiable fractions that are then used to determine the molecule's original configuration. Methods used for fractionating large organic molecules include pyrolysis, chemical cleavage, oxidation, and microreaction. Once the high molecular weight compounds have been reduced to smaller pieces, advanced gas chromatography detectors can be used along with those previously identified to determine the molecule's original structure. High molecular weight, nonpolar molecules are by far the most difficult to define and quantify with current technology.

The future will bring improved techniques for identifying and quantifying organics in water supplies. With this, methods for defining the high molecular weight organics that comprise most of the total organic carbon (TOC) will be defined better. Organic analysis appears to be moving quickly from the present microgram per liter sensitivity to the picogram per liter level. This advanced detection will greatly expand the number of organics of concern in drinking water supplies.

Table 6

Resolution of Organic Compounds From Water: Chromatographic Techniques

Polarity	Volatility							
	Volatile		Semivolatile				Nonvolatile	
Polar	Gas-solid adsorption		Gas-liquid partitioning				Ion-exchange	
Semipolar	Gas-solid partitioning		Liquid-liquid partitioning				Liquid-solid adsorption	
	Gas-solid adsorption		Gas-liquid partitioning				Size exclusion	
Nonpolar	Gas-liquid partitioning						Filtration	
							Size exclusion	
							Permeation	
							Liquid-liquid partitioning	
Molecular Weight	Low		Medium				High	

Table 7

Typical Detection Devices

Polarity	Volatility							
	Volatile		Semivolatile				Nonvolatile	
Polar			Flame ionization				Mutagenicity assay	
			Electron capture				Ultraviolet-visible fluorescence	
Semipolar			Thermionic				Infrared	
			Electrolytic conductivity				Nuclear magnetic resonance	
Nonpolar			Microcoulometric				Pyrolysis	
			Mass spectrometry				Chemical cleavage	
							Oxidation	
Molecular Weight	Low		Medium				High	

4 CHEMICAL TREATMENT/SEPARATION PROCESSES

Overview

Unit processes for removing or destroying organics in a source water vary as a function of the organics' type, species, and concentration. Thus, as with analytical techniques for their evaluation, organics are removed or destroyed in water treatment unit operations through their inherent characteristics--polarity, volatility, and molecular weight.

The concentration of particulate and dissolved organic matter in the raw water can be reduced through improved coagulation, adsorption onto materials such as activated carbon, membrane processes such as ultrafiltration or reverse osmosis, and chemical oxidation. Membrane processes and chemical oxidation are, in general, not cost-effective unless specific toxic organics that are not well suited to adsorption are of concern.

The unit processes mentioned above can be divided into groups that describe the basic mechanism of removal. Although the processes could be grouped in many ways, two categories were chosen: chemical treatment/separation and physical treatment/separation. Table 8 shows these two categories and the removal processes, along with some characteristics of the organic compounds removed. Chemical treatment/separation methods are discussed in this chapter whereas the next chapter covers physical treatment/separation.

Chemical treatment/separation refers to processes that destroy or separate contaminants from water by adding a chemical. These processes, as related to water supply, include chemical coagulation, oxidation, solvent extraction, and adsorption. Since coagulation and oxidation often are standard surface water treatment processes, organic contaminants can be controlled by implementing an operational modification. Thus, if an untreated groundwater source contains organics that require removal, coagulation and oxidation can be considered as alternatives when evaluating treatment processes. This category includes activated carbon, which probably is the technique best suited for treating organic contaminants in raw source waters under the current state of knowledge.

Trihalomethane (THM) Control

Several unit processes and operational strategies suppress THM formation. Since THMs have enforceable drinking water standards and are frequently found in drinking water, there is much laboratory and plant experience in controlling them. Less information is available on plant work to control other organics, but some proven and new treatment processes for removing or destroying them are available.

In February 1983, the USEPA identified five methods representing the "best technology treatment techniques or other means generally available" to achieve compliance with the 0.1 mg/L limit for THMs in drinking water. These methods (Table 8) are almost all aimed at preventing THM formation and are discussed in this report to the extent that they could be used at Army installations. Of these methods, improving existing clarification (settling) to remove precursors, moving the point of chlorination, substituting other preoxidants, and using chloramines are the most promising ways to

Table 8

**Treatment Processes for Organics Removal and Suitable Types
and Characteristics of Compounds Removed**

Treatment/Separation Processes	Types/Characteristics of Compounds Removed
<u>Chemical</u>	
Chemical coagulation	THM and THM precursors, high molecular weight synthetic organics
Oxidation	THM and THM precursors
Clarification	THM and THM precursors
Disinfectant practices	THM
Solvent extraction	Volatile and semivolatile, polar and nonpolar organics, low-medium molecular weight
Adsorption granular-activated carbon (GAC)	THMs, THM precursors, taste- and odor-producing organics, chlorinated hydrocarbon solvents, low-polarity, low solubility compounds
Powdered-activated carbon (PAC)	High molecular weight compounds
Synthetic resins	Chlorinated hydrocarbon solvents, low or high molecular weight, depending on compound of interest
<u>Physical</u>	
Evaporation/volatillization	Low molecular weight, volatile organics
Distillation	High molecular weight, polar, volatile organics
Air-stripping	Moderately volatile organics, some aromatics and pesticides, vinyl chloride, THMs, chlorinated benzene, halogenated organic compounds
Steam-stripping	Moderately volatile, medium molecular weight organics
Membrane processes (reverse osmosis, ultrafiltration)	Higher molecular weight organics, some priority pollutants

control THMs. These methods make use of conventional treatment processes and have been practiced at Army and municipal water treatment plants.

Oxidation/Disinfection--THM Control

Although THMs are the only halogenated organics currently regulated (other than halogenated organic pesticides), they represent only a single class of organic halides produced when raw source waters containing natural and/or synthetic organics are chlorinated during the course of potable water treatment. It has been suggested that total organic halide, as well as THM, formation be minimized.²² One way to do so is by relocating the point of disinfection and/or using alternative disinfectants along with improving the coagulation, flocculation, and separation process, as previously shown in Table 9.²³ This section describes moving the point of disinfection and using alternative oxidants and/or disinfectants, with coagulation strategies discussed in a later section.

Several facilities have moved chlorination to a later step in the treatment process, such as before or after the filters, to reduce the contact time between chlorine and organics. Therefore, since some organics and chlorine-demanding substances are removed in the coagulation/sedimentation process, there are fewer THM forming substances present when chlorine is applied. This allows the dose to be reduced greatly. Of 312 utilities surveyed in 1978, 20 percent do not chlorinate until after sedimentation or filtration.²⁴ A USEPA study of nine utilities showed that the total THM concentration in finished water was reduced by up to 80 percent by delaying chlorination.²⁵ Moreover, an Army Environmental Hygiene Agency (AEHA) study in 1979 at Fort Monroe demonstrated that finished water total THMs were reduced 50 percent by eliminating prechlorination.²⁶ The Louisville, KY, Water Company reduced average total chlorine consumption by about 80 percent as a result of moving the chlorination step to the sedimentation basin outlet, before the softening step. Previously, the chlorine dosage was 120 to 140 lb/MG* and 12 to 15 lb/MG for pre- and postchlorination, respectively. With the new arrangement, only 20 lb/MG are used before the softener and 6 lb/MG after filtration. (Ammonia also is added at both points to create a combined residual.) THM levels once exceeded the MCL, but now they are less than 20 percent of the MCL, according to the Louisville Superintendent of Purification Works.

To take advantage of coagulation, settling, and/or filtration in removing THM precursors, an alternative pretreatment oxidant may be needed to control iron, manganese, taste, odor, and algae. Potassium permanganate, ozone, and chlorine dioxide are all known to be effective oxidants that can be substituted for prechlorination. Potassium permanganate has been shown to be effective in reducing water's chloroform formation potential. These data, however, indicate that effective reductions have been

²²C. D. Cameron, et al., "Organic Contaminants in Raw and Finished Water," *JAWWA*, Vol 68, No. 9 (September 1974).

²³P. A. Chadik and G. L. Amy, "Removing Trihalomethane Precursors from Various Natural Waters by Metal Coagulants," *JAWWA*, Vol 75, No. 10 (October 1983); D. T. Duke, et al., "Control of Trihalomethanes in Drinking Water," *JAWWA*, Vol 72, No. 8 (August 1980).

²⁴AWWA, *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water*, Cooperative Research Report (1983).

²⁵U.S. Environmental Protection Agency (USEPA), *Trihalomethanes in Drinking Water: Sampling, Analysis, Monitoring and Compliance*, EPA 570/9-83-002 (1983).

²⁶AEHA.

*Metric conversions are available on page 82.

Table 9

**USEPA-Identified Methods to Achieve Compliance With
0.1 mg/L MCL for THMs**

- Using chloramines as an alternative or supplemental disinfectant or oxidant.*
- Using chlorine dioxide as an alternative or supplemental disinfectant or oxidant.*
- Improving existing clarification for trihalomethane precursor reduction.*
- Moving the point of chlorination to reduce trihalomethane formation and, when necessary, substitute for chlorine as a preoxidant chloramines, chlorine dioxide, or potassium permanganate.*
- Use of powdered activated carbon for trihalomethane precursor or trihalomethane reduction seasonally or intermittently at dosages not to exceed 10 milligrams per liter on an average annual basis.*

Other methods USEPA says may be considered:

- Introducing offline water storage for trihalomethane precursor reduction.
- Aerating for trihalomethane reduction "where geographically or environmentally appropriate."
- Introducing clarification where not currently practiced.
- Considering alternative sources of raw water.
- Using ozone as an alternative or supplemental disinfectant or oxidant.*

*Indicates method is discussed in this report.

made only at doses considerably higher than those used in typical treatment practice. Typical doses of 0.5 to 2.0 mg/L in the water industry have only a small effect on the overall chloroform production. Use of permanganate as an oxidative pretreatment allows the point of chlorination to be shifted to a postsedimentation or postfiltration location, after a significant amount of organics have been removed by coagulation. It should be recognized, however, that enough contact time must be provided between the point of permanganate application and filtration to allow complete reduction of potassium permanganate to manganese dioxide. If the reaction has not been completed, postfiltration deposition of manganese dioxide may result. Application of permanganate at the intake or rapid-mix chamber should provide enough time for the reaction.

Solid manganese dioxide, produced from the reduction of permanganate, has been shown to be effective as an adsorbant of some organic molecules, thereby providing an additional removal mechanism for organics contained in the source water.²⁷ This phenomenon may particularly apply to facilities that use greensand for iron and manganese removal since the oxidized iron and manganese retained by the greensand coupled with the reduction of the permanganate applied to the filter generate a solid phase with good adsorption properties for humic substances, especially in hard waters. Permanganate appears to have little, if any, impact on the coagulation process and affects only a minor reduction (less than 20 percent) in organics and THM formation potential (THMFP).

Ozone is a very powerful oxidant and is used widely in Europe, where raw waters are of poor quality. It acts more quickly than chlorine as a bactericidal agent and is effective against some viruses.²⁸ Ozone does not combine with organic acids to produce THMs. Ozone has been used to help remove iron and manganese and to break down organics, and some experimental work has demonstrated that ozone pretreatment can help reduce THM levels.²⁹

Other studies suggest, however, that like permanganate, at the doses of ozone commonly used in practice, only modest reductions in organics and THM precursors are realized.³⁰ Also, secondary organics generated by ozonation have not been defined well. Evidence shows that these secondary organics may form chloroform upon chlorination.³¹ However, using ozone instead of prechlorination provides for oxidative pretreatment and disinfection while allowing coagulation to remove significant amounts of organics and THM precursors before final chlorination.

The disadvantage of ozone is that it must be produced onsite by discharging high voltage (5000 to 30,000 V) between electrodes separated by air, requiring a high initial investment for the equipment. (Capital cost is about two-thirds greater than that for chloramines or chlorine dioxide treatment.) Also, it cannot provide enough residual

²⁷ J. E. Dyksen and A. F. Hess III.

²⁸ W. Weber.

²⁹ J. M. Symons, et al., *Treatment Techniques for Controlling Trihalomethanes in Drinking Water*, Technical Report PB 82-163197 (USEPA Municipal Environmental Research Laboratory [MERL], 1981).

³⁰ D. R. Medley and E. L. Stover, "Effects of Ozone on the Biodegradability of Bio-refractory Pollutants," *Journal of the Water Pollution Control Federation (JWPCF)*, Vol 55, No. 5 (May 1983).

³¹ D. R. Medley and E. L. Stover.

disinfection power in the distribution system, so another disinfectant also would be required.

Chlorine dioxide is used most commonly in the United States for controlling taste, odor, and algae, and for removing iron and manganese. In Europe it is used widely as a final disinfectant. The major concern in using chlorine dioxide in potable water treatment has been the formation of chlorite and chlorate as inorganic byproducts of reaction. The health effects of these species is not well understood and, thus, the USEPA has limited total residual concentrations of chlorine dioxide, chlorite, and chlorate to 0.5 mg/L in potable waters.

Chlorine dioxide does not appear to form THMs or other halogenated organics unless free chlorine is present in the chlorine dioxide source. In fact, it appears to reduce the THMFP by up to 50 percent. The prospect of reducing the formation potential for haloforms other than THMs is not well understood at this time.

Like ozone and permanganate, chlorine dioxide is selective in reactivity.³² Unlike chlorine, chlorine dioxide will not react with ammonia and undergoes only limited reactions with amines. This fact has major implications in potable water disinfection since lower dose and longer lasting residuals can be attained using chlorine dioxide. This is possible because nitrogen compounds do not compete for chlorine dioxide as they do for chlorine.

For most water treatment applications, chlorine dioxide is generated by the reaction of chlorine and sodium hypochlorite in solution under acidic conditions:³³



To increase the reaction rate and encourage complete use of the chlorite, an excess of chlorine typically is used. Although this procedure yields the greatest production of chlorine dioxide per unit of the most expensive component, chlorite, it also yields an excess of free chlorine in the product. When chlorine dioxide is applied in the treatment process, then, excess free chlorine will react with the organics to form THMs and other halogenated organics. Thus, the benefit of reduction in THMs and other haloforms using chlorine dioxide is partially offset by the free chlorine byproduct in the chlorine dioxide generation process.

Use of permanganate, ozone, and chlorine dioxide as substitute pretreatment oxidants for chlorine has only a minor effect on THM and other halogenated organic removal at the dosage levels commonly used in potable water treatment. However, using these oxidants as substitutes for chlorine in pretreatment enhances removal of raw organics in the coagulation and subsequent sedimentation and/or filtration unit processes. The resulting reduction in raw organics reduces the formation potential of halogenated byproducts when chlorine is applied for final disinfection. A residual disinfection can be added to the distribution systems using chloramines or chlorine dioxide.

With chloramination, chlorine and ammonia are added in the water treatment and enough reaction time is allowed for the chloramines to form. The pH, temperature, and

³²AWWA, *Treatment Techniques for Controlling Trihalomethanes in Drinking Water*, AWWA Report (1982).

³³G. Culp, *Trihalomethane Reduction in Drinking Water* (Noyes, 1984).

chlorine and ammonia concentrations influence the reactions. If pH is 4.4 or less, nitrogen trichloride, which has a foul odor and poor disinfectant properties, is formed.

Ammonia can be added as ammonium sulfate (25 percent ammonia) with a dry chemical feed system, as anhydrous ammonia (refrigeration gas) fed in solution or diffused in gaseous form, or as aqua ammonia (food-grade) diffused in liquid form. The choice depends on how easily facilities at the treatment plant could be adapted to accommodate ammonia feed. The ammonia dosage is such that the ratio of chlorine to ammonia is 3:1 to 5:1, with a combined chlorine residual of 1 to 2 mg/L achieved.

The Louisville, KY, water company reduced THM levels from a maximum of over 0.2 mg/L to below 0.02 mg/L after switching to chloramination. Prechlorination (20 lb/MG) is done after the coagulation/sedimentation step and to a free chlorine residual of 2 mg/L. Fifteen minutes of contact time are allowed as water flows through a tunnel before 5 to 6 lb/MG of liquid ammonia is added to form monochloramine (pH 6.8 to 7.0). After softening and filtration, 6 lb/MG of chlorine and 1.6 lb/MG of liquid ammonia are added to produce a combined chlorine residual of 1.5 mg/L in the distribution system, according to Louisville officials. The system is flushed when standard plate counts of bacteria at various points in the distribution system exceed predetermined levels. With this program, THMs and bacteria are controlled.

At one Army installation, prechlorination of raw water to 1.5 to 2 mg/L free available chlorine provides a residual of 0.1 mg/L through the sedimentation basin to prevent algae growth. After filtration and pH adjustment, chlorine and ammonia are added in a ratio of about 5:1 to provide a total residual of 2.6 mg/L in the finished water. Anhydrous ammonia is added just before the chlorine to keep additional THM formation to a minimum. With this practice, THMs have been brought well below the MCL. A flushing program is carried out to keep lines free of bacteria and algae, and bacteriological samples are taken regularly. The flushing program at this installation is necessary because of high algae levels in the raw water.

Table 10 compares costs for three sizes of water treatment plants with conventional prechlorination and with alternative pretreatment disinfectants. In selecting any alternative(s) for mitigating organic contamination of a potable water supply, it should be recognized that the finished potable water must be disinfected properly and that water in the distribution system must be protected adequately.

Decomposing Organics by Ozonation

Ozone is recognized for its ability to treat wastewater-containing organic matter and other contaminants. Laboratory tests have demonstrated that ozone can break down complex organic compounds.³⁴ It has been used to treat hydrocarbon wastes in rubber plants, refineries, and solvent manufacturing plants.³⁵ Ozone has had infrequent use in disinfection and taste and odor control in potable water treatment plants; one example is the town of Whiting, IN, which has used ozonation since the 1940s to treat drinking water

³⁴P. S. Bailey, "Organic Groupings Reactive Toward Ozone: Mechanisms in Aqueous Media," *Ozone in Water and Wastewater Treatment* (Ann Arbor Science, 1972); AWWA, *Water Reuse Highlights* (1978).

³⁵U.S. Department of the Interior, *Characteristics and Pollutational Problems Associated With Petrochemical Waste* (Federal Water Pollution Control Administration, February 1970).

Table 10

**Cost Estimates for Alternatives to Prechlorination
(Cents/1000 Gal)***

	<u>1 MGD</u>	<u>5 MGD</u>	<u>10 MGD</u>			
	A	B	A	B	A	B
<u>Chlorination**</u>						
1 ppm dose	2.8	3.7	0.8	1.1	0.5	0.7
3 ppm dose	3.6	5.2	1.2	1.6	0.9	1.2
6 ppm dose	4.3	6.2	1.7	2.3	1.4	1.8
<u>Chloramination**</u>						
0.75 ppm chlorine dose	4.9	5.8	1.5	1.8	0.9	1.1
1.5 ppm chlorine dose	5.9	6.9	1.8	2.2	1.2	1.5
2.2 ppm chlorine dose	7.2	8.4	2.2	2.7	1.5	1.8
<u>Chlorine dioxide**,***</u>						
1 ppm dose	5.6	6.6	2.5	2.8	2.0	2.2
3 ppm dose	9.0	10.3	5.6	6.1	4.9	5.2
<u>Ozonation+</u>						
(10 min contact time)						
1 ppm dose		6.9		3.5		2.3
3 ppm dose		10.4		5.5		4.0

*Case A--Chlorination feed system exists. New feed system for chemicals in question.
Case B--New chlorine and other chemical feed systems. All costs shown include capital (where new facilities are indicated), operating and maintenance costs, assuming 70 percent plant capacity, 20-year amortization period, and 8 percent interest. ENR Construction Cost Index = 369.80 (January 1983) and Producer Price Index--Finished Goods = 283.6 (January 1983). Chlorine costs \$300/ton, ammonia costs \$200/ton. Chlorine to ammonia ratio is 3:1.

**Based on *Evaluation of Treatment Effectiveness for Reducing Trihalomethanes in Drinking Water*, USEPA Contract No. 68-01-6292 (1983), pp 98-102.

***Sodium chlorite costs \$2000/ton. Contact time is 20 min.

+Costs projected from 1980 costs given in earlier USEPA publication, *Treatment Techniques for Controlling Trihalomethanes in Drinking Water* (USEPA, MERL [September 1981]).

for taste and odor.³⁶ The 1.5 to 2.0 million gallons per day (MGD) plant has an ozone generation capacity of 75 lb/day. The ozonation is used during pretreatment and is especially advantageous when the raw water contains phenols or petrochemical compounds. Several other cities use ozonation to remove unwanted taste and odor caused by these organics.

In removing organic compounds, ozone (O_3) acts as an oxidizing agent and, if the ozone dosage and contact time are long enough, the organic matter is broken down to harmless carbon dioxide and water. Conditions seldom are suitable or practical enough to achieve this condition for all the organics of concern. Instead, partially oxidized intermediate organic compounds may form. These compounds' toxicity and health effects are unknown at present; however, they often are more biodegradable or more easily adsorbed onto a medium.³⁷ This knowledge expands the potential for using ozone in combination with other treatment processes; one example of this combined technology is at a wastewater treatment plant in Cleveland, OH.³⁸ After ozonation at this plant, the water is filtered and applied to a granular-activated carbon (GAC) bed. The intermediate organic compounds are absorbed more readily in the activated carbon bed and thus are more soluble and biodegradable than in other treatment systems. A similar system could be used at a potable water treatment plant; Figure 5 is a schematic for such a system.³⁹ The multimedia filter and aeration tank following the ozone contactor are optional. Biodegradation and adsorption occur in the granular-activated carbon column, adding the benefit of not having to regenerate the carbon as often.

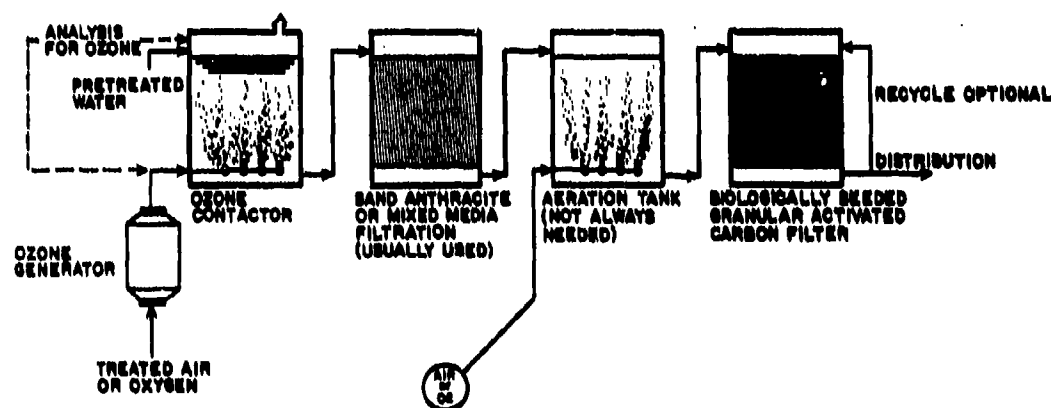


Figure 5. Ozonation/biological-activated carbon system. (From: M. Schwartz, R. Rice, and A. Benedek, "A Study of the Feasibility to Achieve Reusable Water by Ozonation/Biological-Activated Carbon Technology," *Water Reuse Symposium II Proceedings*, Vol 2 [AWWA Research Foundation, 1981]. Used with permission.)

³⁶ R. P. Oulette, et al., *Electrotechnology, Vol I: Wastewater Treatment and Separation Methods* (Ann Arbor Science, 1978).

³⁷ AWWA, 1978; M. Schwartz, R. Rice, and A. Benedek, "A Study of the Feasibility to Achieve Reusable Water by Ozonation Biological Activated Carbon Technology," *Water Reuse Symposium II Proceedings*, Vol 2 (AWWA Research Foundation, 1981).

³⁸ R. P. Oulette, et al.

³⁹ M. Schwartz, R. Rice, and A. Benedek.

Potable water treatment plants in Europe have used ozone/GAC for several years and, at plants where biodegradable has been effective, the GAC media did not have to be regenerated for 3 years.⁴⁰ Pilot plant studies in the Netherlands using ozone/GAC treatment demonstrated that the two processes together removed taste- and odor-producing compounds more effectively than either process alone.⁴¹ The system using ozone followed by biologically activated GAC probably will undergo further testing before design specifications and cost data are available, but it does show promise for removing organics from potable water.

Another technology for removing organics is ultraviolet (UV)/ozone treatment. In order to completely break down chlorinated hydrocarbons, for example, solvents and pesticides that do not break down easily in the environment, the carbon-chlorine bonds must be broken. Ozonation alone will not do this, but if UV light and ozone are applied, these bonds break and the organic compounds decompose more quickly. The UV/ozone system has been laboratory-tested on aliphatic and aromatic hydrocarbons and was found to decompose these compounds more effectively than if ozone alone were used.⁴² UV/ozone treatment thus has potential application in organics removal from potable water but further laboratory and pilot testing is needed to develop design and operating specifications as well as cost estimating methods. Table 10 shows overall costs for 1- and 3-ppm dosages of ozone for 1-, 5-, and 10-MGD plants.

Chemical Coagulation

Chemical coagulation/flocculation is effective for removing humic acids, which are precursors for THM formation. Coagulation/flocculation has not been as effective for removing volatile (petroleum-based) organics and limited work has been done to evaluate how well other synthetic organic compounds are removed. For these reasons, chemical coagulation is discussed with respect to its potential for helping to control THMs.⁴³

Coagulation has several advantages over granular activated carbon adsorption, including little additional capital investment, minor increase in unit-process operating cost, and reasonably well defined technology (relative to other systems).⁴⁴ However, coagulation is less effective than the other alternatives, and jar and plant tests should be conducted to see if this method reduces precursor organics well enough.

Conventional treatments such as turbidity removal and softening have been shown to remove some organic acids (THM precursors) and thus help control THM levels in the

⁴⁰ M. Schwartz, R. Rice, and A. Benedek.

⁴¹ W. C. VanLier, et al., "Experience With Granular Activated Carbon Filters on Pilot Plant Scale," *Activated Carbon in Drinking Water Technology* (AWWA Research Foundation, 1983).

⁴² E. Leitis, et al., "The Chemistry of Ozone and Ozone/UV Light for Water Reuse," *Water Reuse Symposium II Proceedings*, Vol 2 (August 23-28, 1981).

⁴³ R. R. Trussell and A. R. Trussell, "Evaluation and Treatment of Synthetic Organics in Drinking Water Supplies," *JAWA*, Vol 72, No. 8 (August 1980); O. T. Love and R. G. Eilers, "Treatment of Drinking Water Containing Trichloroethylene and Related Industrial Solvents," *JAWWA*, Vol 74, No. 8 (August 1982); U.S. Department of the Interior.

⁴⁴ R. M. Clark, et al., "GAC Treatment Costs: A Sensitivity Analysis," *American Society of Civil Engineers, Environmental Engineering Division Journal (ASCE/ EEDJ)*, Vol 110, No. EE4 (August 1984).

finished water. A field study of 10 utilities using Ohio River water determined that the conventional treatment processes removed from 29 to 51 percent of the THM precursors.⁴⁵ In addition, an unpublished USEPA study of a lime-softening plant in Daytona Beach, FL, measured a 27 to 43 percent reduction in finished water THM levels (compared to chlorinated raw water with no further treatment, depending on where chlorine was added). If these processes at Army water treatment plants could be optimized to remove THMs and their precursors, considerable savings could be realized in cases for which more costly, sophisticated THM control measures would otherwise be needed.

Adjusting the type of coagulant, dosage, and pH has been shown to improve removal of organic acids during coagulation and sedimentation. It is not known how organics are removed during coagulation, but unpublished experiments have shown that the order of chemical addition as well as mixing speed and time do not influence organics removal when conventional coagulants are used. The coagulant dose, pH, and type of organic acids present are the most important factors determining the efficiency of organics removal.

One set of tests using Mississippi River water showed that an alum dosage of 100 mg/L at pH 5 was best for achieving a 85 percent reduction in THM levels. At the same pH, a 25-mg/L alum dose yielded 35 percent removal.⁴⁶

The USEPA has studied the use of polymers in improving organics removal during coagulation/sedimentation. Mississippi River water was subjected to jar tests with various combinations of coagulants and coagulant aids, using UV absorbance as an indicator of organics removal. Adding a cationic polymer (2 mg/L) to an alum or ferric sulfate coagulant increased organics removal from raw water when the coagulant dosage was at the optimal dosage (unpublished results). For a given polymer type, those of higher molecular weight were superior. Nonionic and anionic polymers used as coagulant aids did not improve organics removal.

A polymer is being used at one Army installation as a coagulant aid to control THMs. Approximately 1 mg/L is mixed and fed continuously through a chemical feed pump at the rapid mixers. THM levels before using the polymer exceeded the 0.1 mg/LMCL; levels in the distribution system decreased within 1 day after beginning the treatment and are now below 0.1 mg/L. Other benefits of using the polymer are that it improves settling and eliminates the need to add another coagulant aid previously used.

In the USEPA unpublished study mentioned above, addition of clay (10 mg/L) to a cationic polymer (with the polymer used as primary coagulant) prevented suspended matter from restabilizing, enabling 40 percent organics removal at primary coagulant dosages from 5 to 20 ppm. When both clay (10 mg/L) and a cationic polymer were used along with the optimal dosage of ferric sulfate, organics removal again increased. In that case, cationic polymer dosages were less than 5 mg/L.

Lime softening will remove some organics. The USEPA found in the study using UV absorbance to indicate organics removal, that at lime dosages above the stoichiometric dosage, the organics concentration was decreased by 36 percent. When 20 mg/L alum or

⁴⁵J. M. Symons, et al., *Treatment Techniques for Controlling Trihalomethanes in Drinking Water*.

⁴⁶M. J. Semmens and T. K. Field, "Coagulation: Experiences in Organics Removal," *JAWWA*, Vol 72, No. 8 (August 1980).

Iron was added, the indicator showed that organics removal improved to 64 percent. Another USEPA study showed that the range of precursor removal in lime precipitative softening is from 16 to 41 percent.⁴⁷

Evaluating How to Improve Coagulation

The potential for successful mitigation of organic precursors using chemical coagulation requires the design engineer answer four basic questions:⁴⁸

1. What level of TOC must be achieved to meet existing or anticipated organics criteria?
2. Can this requisite treatment level be attained using coagulation?
3. What combination of coagulants, coagulant aids, and physical/chemical (pH, temperature, etc.) characteristics yields the greatest reduction in organics?
4. What additional capital and operational/maintenance costs are associated with implementing this strategy?

These questions often can be answered only by onsite evaluation using treatability techniques. How existing coagulation/sedimentation or softening processes could be modified to improve organics removal will depend on the existing equipment at the installation, the raw water's characteristics, and the magnitude of the THM problem. In the two studies just noted, THM precursors were removed by varying coagulant or lime dosage, varying pH, using coagulant aids, and changing the point of chlorination. Jar tests should be conducted when determining which modification involving chemicals would improve organics removal. UV absorbance measurements before and after the jar test can be used to indicate organics removal. In addition, Table 11 shows different ways of determining how to improve clarification to control THMs.

As another way of improving coagulation, once the appropriate coagulant dosage is determined, a cationic polymer (approximately 2 mg/L) or clay (approximately 10 mg/L) plus a cationic polymer (0 to 5 mg/L) could be jar-tested. Using a polymer may widen the pH range corresponding to the optimal coagulant dosage for both organics and turbidity removal.

Increasing the lime dosage beyond stoichiometric levels and adding alum or iron to improve organics removal during softening also could be evaluated using jar tests, measuring UV absorbance before and after treatment. In conducting these tests, it should be remembered that the investigation is concerned with the dosage-response relationship for the organic and not with other contaminants such as turbidity.⁴⁹ Therefore, the best dosage combination for organics removal may not coincide with that for turbidity or other classic indicators. Figure 6 shows how results of jar tests using various dosages of alum at a range of pH levels can be used. THM concentration and

⁴⁷J. M. Symons, et al., *Treatment Techniques for Controlling Trihalomethanes in Drinking Water*.

⁴⁸P. A. Chadik and G. L. Amy; S. P. Shelton and W. A. Drewry, "Tests of Coagulants for the Reduction of Viruses, Turbidity, and Chemical Oxygen Demand," *JAWWA*, Vol 65, No. 10 (October 1973).

⁴⁹S. P. Shelton and W. A. Drewry.

Table 11

Determining How to Improve Existing Clarification
to Control THMs

Jar Tests

Use UV absorbance as indicator of organics removal

Vary coagulant or lime dosage

Vary pH

Try cationic polymer or clay plus cationic polymer

If using lime, try adding alum or iron

Plant Tests

Measure THM levels in raw and finished water for normal
treatment and with modification

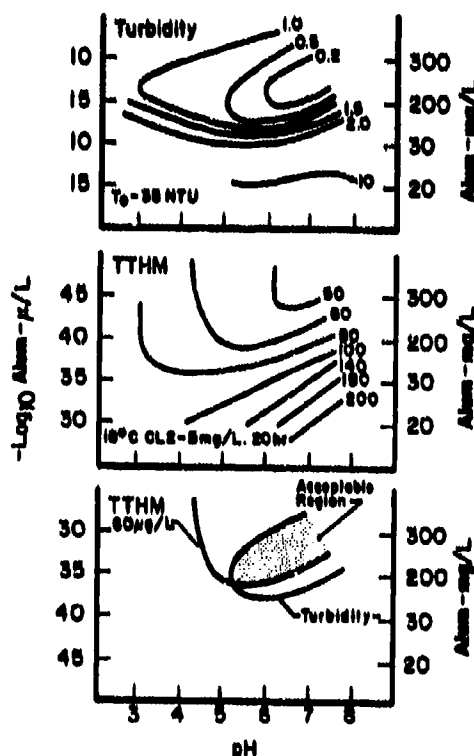


Figure 6. Determining optimal dosage and pH for organics and turbidity removal.
(From: R. R. Trussell and A. R. Trussell, "Evaluation and Treatment of
Synthetic Organics in Drinking Water Supplies," JAWWA, Vol 72, No. 8
[AWWA, August 1980]. Used with permission.)

turbidity each are plotted on separate graphs for the various coagulant dosages and pH levels tested. The two plots are superimposed to determine the optimal dosage and pH to control both.

Once the new coagulant and/or lime dosage, pH, and effectiveness of coagulant aids have been determined in the laboratory, they could be tested in the plant. For a complete evaluation, samples of the raw and finished water should be taken during (1) existing operation and (2) the test. However, if the desired reduction of organic contaminant cannot be obtained in the laboratory, this is strong indication that a more vigorous unit process (e.g., activated carbon, air-stripping) will be required to meet the organic criteria.

Table 12 compares costs for several dosages of alum and polymer needed to treat water in meeting the THM regulation.⁵⁰ Local costs may vary, but jar or plant test results could be used similarly to estimate treatment costs based on the required dosage of the alternative chemicals.

The efficiency of coagulation for organic/organic-precursor removal depends on the type and concentration of organic compounds in the water supply, pH, coagulant dosage, and the solids/liquid separation step.⁵¹ Preferred conditions for organics removal must be determined by batch studies and should be confirmed in plant-scale tests if possible. In some instances, the water chemistry may demand residual TOC levels below those achieved economically by coagulation. It has been demonstrated and documented in the literature that TOC levels in the 1 mg/L range can be reached using coagulation.⁵² The minimum TOC must, however, be determined for each source water by jar-test evaluation. Coagulation offers the major advantage of reduced unit cost and can be used when TOC levels on the order of 2 mg/L are required. For these conditions, improved coagulation and alteration of the chlorine dosage point may provide a finished water of suitable organic quality at minimal increase in unit operating cost.

The applicability of coagulants and alternative oxidants and disinfectant strategies for removing THM and other haloform precursors has been widened. It is possible that with proper pH control, classic aluminum and iron salt coagulants can remove substantial amounts of raw organics that would otherwise form halogenated organics when chlorinated.⁵³

Solvent Extraction

Solvent extraction partially separates water's liquid constituents into two immiscible liquid phases. This process occurs because of the constituents' different solubilities and is highly effective for extracting specific organic species from water; it has long been used effectively in both laboratory and industrial process applications.⁵⁴ The petroleum industry also has used the solvent extraction principle to remove phenols from wastewater.

⁵⁰ *Evaluation of Treatment Effectiveness for Reducing Trihalomethanes in Drinking Water*, USEPA Contract No. 68-01-8292 (July 1983).

⁵¹ S. P. Shelton and W. A. Drewry.

⁵² P. A. Chadik and G. L. Amy.

⁵³ S. P. Shelton and W. A. Drewry.

⁵⁴ S. P. Shelton, et al., *RCRA Risk/Cost Policy Model*, USEPA/OSW Report (June 1982).

Table 12

**Estimated Cost of Increased Alum and Polymer Dosages
to Meet THM MCL***

	Increased Dosage (mg/L)	Cost in \$/m ³ (¢/1000 gal)
<u>Alum**</u>		
	10	0.16 (0.60)
	20	0.32 (1.20)
	30	0.48 (1.70)
	40	0.61 (2.30)
	50	0.77 (2.90)
<u>Polymer***</u>		
	0.2	0.11 (0.40)
	0.4	0.21 (0.80)
	0.6	0.34 (1.30)
	0.8	0.48 (1.70)
	1.0	0.55 (2.10)

*Cost includes only that for additional chemicals. No additional capital facilities or O&M requirements are included. Based on *Evaluation of Treatment Effectiveness for Reducing Trihalomethanes in Drinking Water*, USEPA Contract No. 68-01-6293 (July 1983), p 108.

**Assumed alum cost \$140/ton.

***Assumed polymer cost \$2.50/lb.

A mixer-settler combination is used most commonly for large-scale operations. The baffled mixing vessel contains a rotating impeller for dispersing the solvent uniformly. In the treatment process, the vessel is first filled with the organic-contaminated water and then is mixed with solvent. When the water/solvent mix becomes homogeneous at a solvent/water ratio of 25 to 75 percent, depending on organic species and solvent characteristics, the mixture is transferred to a decanter in which the two phases separate. When separation is complete, the extract containing the organic species of concern is removed and the remaining liquid layer is the treated water. This process can be done in a batch or continuous mode.

Liquid-liquid extraction is an effective treatment technique that can remove high levels of a broad range of organic species. However, it is also a very expensive process per unit of organic-free water produced.⁵⁵ Furthermore, the organic-containing solvent must be treated and reused, and the effectiveness of this regeneration is a function of the organic species removed from the water and the solvent. In many cases, it is not practical to reduce the organics in solvent to a level low enough for solvent reuse. For these reasons, liquid-liquid extraction is not used as a unit process for removing organic species from potable water supplies. It is of interest in this report only because the combination of more stringent water quality regulations along with advances in the technology may make it a feasible process in the future.

⁵⁵S. P. Shelton, et al., 1982.

Biodegradation

Biodegradation as a way of removing organic compounds has been studied in the laboratory, with most work focusing on removal from wastewater.⁵⁶ In experiments using bacteria under aerobic and anaerobic conditions, certain hydrocarbons did degrade, including carbon tetrachloride, TCE, and PCE. Under anaerobic conditions, the organic compounds may be transformed according to the following pathways:

- Carbon tetrachloride to chloroform to methyl chloride.
- PCE to TCE to dichloroethylene to vinyl chloride.
- 1,1,1-Trichloroethane to 1,1-dichloroethane to chloroethane.

The petroleum industry has studied the potential for biodegradation of organic compounds in its wastewaters. These findings provide general observations about biodegradation:⁵⁷

- Aliphatic compounds and cyclic aliphatics are more biodegradable than aromatic compounds.
- Unsaturated aliphatics (such as acrylic, vinyl, and carbonyl compounds) generally are biodegradable. Organic compounds that have a molecule other than carbon on the primary chain are not as susceptible to biological breakdown.
- Chlorinated hydrocarbon pesticides generally are not biodegradable.
- Molecular size and solubility are important factors. Larger, less soluble compounds are more difficult to break down.
- Adding or removing a functional group affects the biodegradability. For example, if a hydroxyl or amino group is substituted for a halogen on a benzene ring, the benzene compound is less biodegradable.
- Mixtures of more than one organic compound may influence the biodegradability of the individual compounds.

Activated Carbon Adsorption

The use of activated carbon to adsorb organic materials from water has become well established as a practical, reliable, and economical unit process.⁵⁸ This is the preferred approach for control of organics that generate color, odor, or haloforms, and other organic contamination in potable water supplies. Historically, macrolevel organics have been removed in the typical surface-water treatment facility by coagulation, flocculation, sedimentation, and filtration.⁵⁹ These processes are, however, often unable to remove enough trace organics to meet existing potable water criteria for THMs and

⁵⁶U.S. Department of the Interior.

⁵⁷U.S. Department of the Interior.

⁵⁸R. M. Clark, et al.; J. H. Geraghty and D. W. Miller, "Adsorption of Organics From Domestic Water Supplies," JAWWA, Vol 70, No. 3 (March 1978).

⁵⁹S. P. Shelton and W. A. Drewry.

pesticides. As the number and types of regulated organic species in water supplies expand with improved analytical techniques and as new suspected or confirmed carcinogens are discovered, carbon adsorption will become more prevalent as a unit process in potable water treatment. Organic compounds that have a high molecular weight and are less soluble are more easily adsorbed on activated carbon. Also, unsaturated organic compounds such as ethanes are more easily adsorbed than saturated ones such as ethane.⁶⁰

Upon contact with water-containing soluble organic materials, activated carbon removes these materials selectively by adsorption. The use of surface energy to attract and hold molecules is called "physical adsorption." Since activated carbon has an extremely large surface area per unit weight (approximately 1000 m²/g), it is an efficient adsorptive material. In manufacturing activated carbon, many pores are generated within the particles resulting in vast areas of walls within these pores, which accounts for the extraordinary surface area-to-volume ratio. Thus, activated carbon can adsorb a wide range of organic species, including the nonpolar, high-molecular-weight molecules that are not controlled well by other unit processes.

Carbon size affects the rate of organic adsorption but not the total adsorption capacity.⁶¹ Thus, the two types of carbon adsorption processes discussed in this section, granular and powdered, are similar in per-unit adsorption capacity, with the powdered carbon having a higher rate of adsorption.

Water quality parameters other than organics affect the adsorptive capacity and life of activated carbon systems. Specifically, pH levels above 9.0 reduce the carbon's adsorptive capacity substantially. In addition, suspended solids and colloidal materials often reduce carbon life by restricting the pore openings, thereby reducing the adsorption capacity.

In current applications, GAC usually is produced from select grades of coal. These carbons are hard, dense, and abrasion-resistant. They are amenable to slurry transport and repeated handling during regeneration without significant deterioration. Although many different sizes of GAC have been used successfully, the three most typical ranges are 8 X 30 mesh, 12 X 40 mesh and 20 X 40 mesh. The 20 X 40 size means that the GAC will pass through the U.S. Standard Mesh Size No. 20 (0.03 in.) but will be retained on a No. 40 size mesh (0.017 in.). The finer material has a higher adsorption rate, but also a higher head loss per unit depth of bed. Furthermore, since beds have lower porosity, they have a greater tendency to foul by collecting colloidal materials from the water. Conversely, the 8 X 30 mesh has a lower adsorption rate, lower head loss per unit depth of bed, and withstands regeneration with fewer losses. Both are good carbons; the designer must select one based on characteristics of the water to be treated. Since bed life and suspended solids load are less critical for GAC applications in potable water treatment than in wastewater or industrial waste treatment, adsorption rate may dominate the GAC size selection process. Powdered-activated carbon (PAC) usually is considered to be smaller than 50 mesh. The adsorption rate for PAC systems is very high; however, unit processes that use PAC have not evolved such that carbon recovery is as straightforward as for GAC systems. Both unit process types are discussed in more

⁶⁰J. E. Dyksen and A. F. Hess.

⁶¹W. Weber.

detail after the following explanation of absorption isotherms--a principle important in understanding GAC and PAC.

Adsorption Isotherms

Regardless of the carbon type, the adsorption effectiveness of activated carbon on the organic species of concern is a key to developing design data for either type of carbon adsorption system. Much research has been done in developing procedures for determining adsorption capacity.⁶² Using one such procedure, a carbon's adsorptive capacity can be measured to a reasonable degree when the adsorption isotherm is determined experimentally for the system under consideration. "Adsorption isotherm" is the relationship, at a given temperature, between the amount of a substance adsorbed and its concentration in the surrounding solution.

Using a color adsorption isotherm as an example, the adsorption isotherm would consist of a curve plotted with residual color in the water as the abscissa and the color adsorbed per gram of carbon as the ordinate. Data taken at any point on the isotherm yields the color adsorbed per unit weight of carbon, which is the carbon adsorption capacity for that color concentration and temperature. Figure 7 shows a typical isotherm for removing a contaminant by four different carbon types, A, B, C, and D.⁶³ Carbon A lies above carbon B and is a better choice because it adsorbs more of the

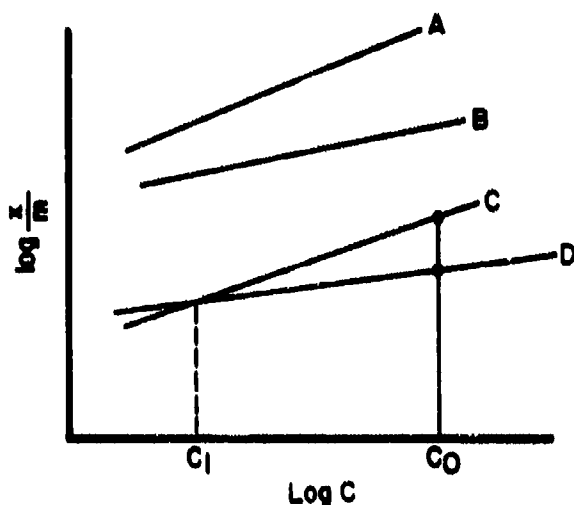


Figure 7. Adsorption isotherms for four carbons. (From: L. D. Benefield, J. F. Judkins, and B. L. Weand, *Process Chemistry for Water and Wastewater Treatment* [Prentice Hall, 1982]. Used with permission of the Chemical Publishing Co.)

⁶²W. Weber; C. Oulman, *Trace Organics Study, Vol 3, Trace Organics Removal Using Activated Carbon and Polymeric Adsorbents*, ISU-ERI-AMES-80189 (Engineering Research Institute, Iowa State University, Ames, 1980); J. C. Kruithof, "Evaluation," *Activated Carbon in Drinking Water Technology* (AWWA Research Foundation, 1983).

⁶³L. D. Benefield, J. F. Judkins, and B. L. Weand, *Process Chemistry for Water and Wastewater Treatment* (Prentice-Hall, 1982).

compound per unit weight of carbon. A carbon with a steeper isotherm usually is preferable to a carbon with a flat isotherm because the adsorptive capacity is higher at higher equilibrium concentrations.

Comparing curves C and D, carbon C is preferable if the system will be operated at an equilibrium organic concentration (in the treated water) above C_1 . In a dilute system such as potable water, the relationship typically is logarithmic and, thus, the Freundlich equation, which relates the amount of contaminant remaining to the contaminant adsorbed, has found widespread use. This equation is expressed as:

$$\frac{X}{M} = KC^{1/n} \quad [\text{Eq 2}]$$

where: X = Amount of contaminant adsorbed

M = Weight of the carbon

K, n = Constants

C = Amount of contaminant remaining in solution.

The logarithmic form of this equation is:

$$\log \frac{X}{M} = \log K + \frac{1}{n} \log C$$

Thus, if the relationship is logarithmically linear, $1/n$ represents the slope of the line, which is used to interpret the removal effectiveness of that carbon for the contaminant measured at that temperature. Figure 8 shows GAC isotherms for several organic compounds, most of which have proposed drinking water standards.⁶⁴ The USEPA *Treatability Manual* also contains isotherms for several organic compounds.⁶⁵ Isotherms from published sources may be used for guidance and preliminary studies. For design purposes, isotherms should be determined from tests with GAC under consideration and the water to be treated.

Classic carbon capacity tests, such as those for the iodine and molasses numbers, may indicate the adsorption capacity of a carbon contemplated for a specific use. The iodine number represents milligrams of iodine adsorbed from a 0.02-N solution at equilibrium under specified conditions. The molasses number is an index of the carbon's adsorptive capacity for color bodies in a standard molasses solution as compared to a standard carbon. These numbers can be used for carbon-type screening as a function of the organic species of concern. Specifically, iodine number reflects the carbon's efficiency for adsorbing small molecules; molasses number predicts the carbon's affinity for large organic molecules.

The potential for removing both gross organics and specific organic species can be determined from an isotherm test. Furthermore, the procedure will indicate the carbon's

⁶⁴V. Snoeyink, "Control Strategy--Adsorption Techniques," *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water* (AWWA Research Foundation, 1983).

⁶⁵USEPA, *Treatability Manual* (Office of Research and Development, September 1981).

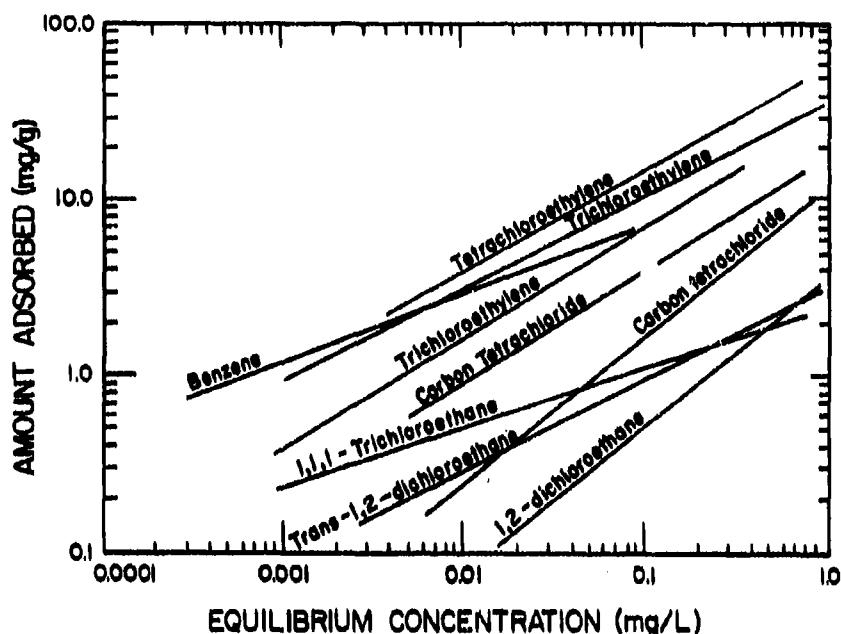


Figure 8. Adsorption isotherms for organic contaminants. (From: V. Snoeyink, "Control Strategy--Adsorption Techniques," *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water* [AWWA Research Foundation, 1983]. Used with permission.)

approximate capacity for the specific application and provide a preliminary estimate of the carbon dosage required. For example, an approximation of the amount of carbon consumed per day would be equal to the amount of contaminant to be removed per day, divided by the carbon's adsorptive capacity. Figure 9 shows a design example using an adsorption isotherm. It should be noted that this isotherm is unique to a particular carbon, water to be treated, temperature, and pH. Isotherm tests also provide a convenient way to evaluate the effects of pH and temperature on adsorption. Isotherms concentrate a large volume of data into a concise format suitable for evaluation and interpretation.

Granular-Activated Carbon (GAC)

GAC has been a popular choice for removing organics from potable water. In discussing GAC beds, several design and operating parameters should be defined, as summarized in Table 13. The adsorption isotherm was just discussed. Another parameter, breakthrough curve, shows the contaminant concentration in the effluent plotted against the water volume treated, as Figure 10 shows.⁶⁶ As water filters through the bed, carbon adsorbs the organic compound. Gradually, all adsorption sites are filled and the compound appears in the effluent. The effluent concentration then may exceed the allowable level (C_B in Figure 10) and the breakthrough point is reached. The point at which the contaminant concentration in the effluent is 95 percent of the influent concentration is called the "point of exhaustion," denoted at C_E . Curve a in Figure 10 is steep, meaning the water caused the bed to reach exhaustion soon after breakthrough.

⁶⁶L. D. Benefield, J. F. Judkins, and B. L. Weand.

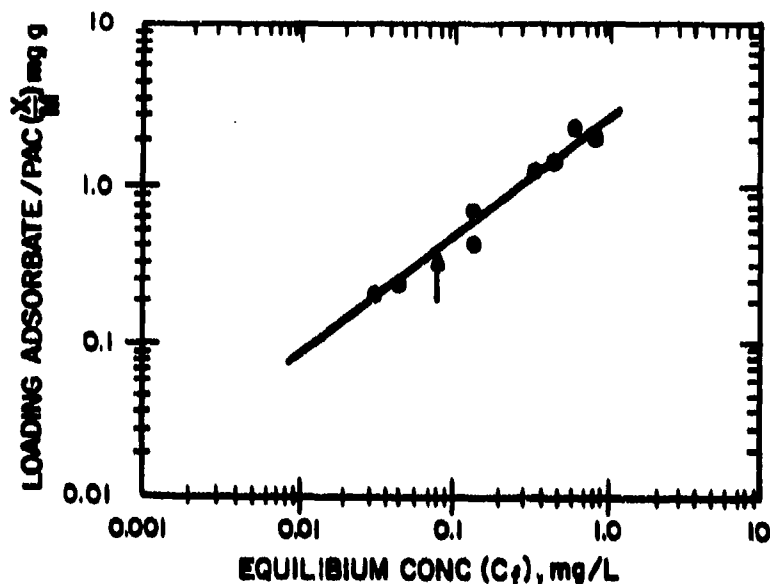


Figure 9. Example adsorption isotherm for determining PAC dosage for chloroform removal from a water using Filtersorb 300. (From: J. M. Symons, et al., *Treatment Techniques for Controlling Trihalomethanes in Drinking Water* [USEPA, 1981]. Used with permission.)

Table 13

Design and Operating Considerations for GAC Plants

Adsorption isotherm (slope of line)

Shape of breakthrough curve

Time of exhaustion

Bed depth

Empty bed contact time (EBCT) = GAC bed volume/flow

Carbon usage rate (mg/L or lb/1000 gal) = mass of carbon used/volume of water treated at breakthrough point

Loading rate (bed volumes) = total volume of water treated at breakthrough point/GAC bed volume

Linear velocity = flow/bed area

Backwashing frequency

Carbon regeneration - frequency and cost

Location in treatment plant

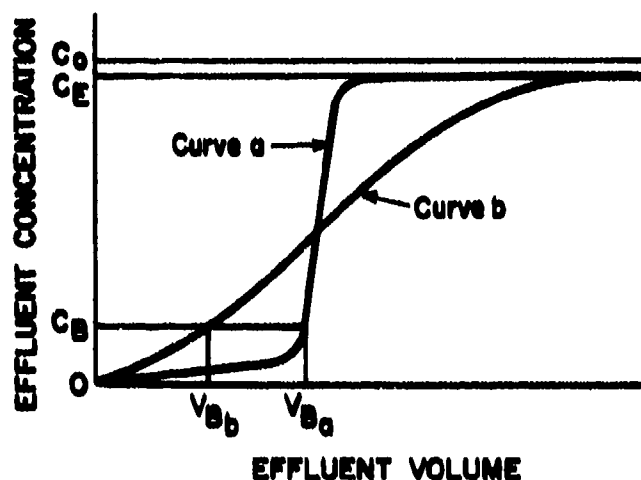


Figure 10. Breakthrough curves. (From: L. D. Benefield, J. F. Judkins, and B. L. Weand, *Process Chemistry for Water and Wastewater Treatment* [Prentice-Hall, 1982]. Used with permission.)

This is often characteristic of water with only one contaminant being adsorbed.⁶⁷ Curve b describes a water with more than one contaminant being adsorbed on the carbon.

Another important parameter in discussing GAC adsorption is empty bed contact time (EBCT), defined as:

$$\text{EBCT} = \frac{\text{Volume of GAC in bed or column}}{\text{flow of water}} \quad [\text{Eq 3}]$$

EBCT usually is about 10 min, but can range from 9 to 54.5 min.⁶⁸ Factors affecting EBCT are the carbon's type and size, organic compound concentration in the influent, flow rate, and bed depth. Bed depth may range from about 2 to 14 ft,⁶⁹ and is also an important design variable since it influences the expense for carbon.

Other process variables are carbon usage rate (expressed in mg/L or lb/1000 gal), loading (often expressed in terms of bed volumes), and linear velocity or application rate (flow divided by cross sectional area). Typical loading rates of GAC plants in The Netherlands are 14,000 to 55,000 bed volumes and linear velocity ranges from less than 1 to 1.6 ft/min.⁷⁰ Flow rates range from 2 to 10 gpm/sq ft.

⁶⁷L. D. Benefield, J. F. Judkins, and B. L. Weand.

⁶⁸J. C. Krulthof.

⁶⁹V. Snoeyink.

⁷⁰J. C. Krulthof.

Backwashing frequency is an important operating parameter for gravity GAC beds. Plants try to backwash as seldom as possible so as not to disturb the bed. Some operations do not backwash at all, whereas others backwash about once per week.⁷¹

Regeneration also contributes to total operating costs. Regeneration frequency will be determined by the water's character and operating parameters, and the cost for regeneration will vary by locality. Regeneration is done an average of every 15 months and about 5 to 10 percent of the carbon is lost.⁷² Another option is to use GAC that is not regenerable.

Finally, the GAC contactors' configuration and location in the treatment plant must be considered. GAC beds or columns can be installed as a single column (usually adequate for small flows), in series, or in parallel, depending on the amount and quality of water to be treated. The GAC process usually is positioned at the end of the treatment process, after turbidity removal, softening, and iron and manganese removal. Most GAC processes are preceded by rapid filtration to remove fine, precipitated matter that could clog pores in the GAC.

GAC can be used in either of two ways: (1) removing some of the sand in an existing rapid sand filter and replacing it with GAC or (2) as carbon columns with pretreated water being passed through a GAC column. The advantage of capping existing sand filters with GAC is low cost.⁷³ The process, however, does require careful investigation of the carbon contact time necessary to remove the organic species since the filter beds are shallow. Furthermore, carbon losses due to backwash and the logistics of removing the GAC cap for regeneration give the process major operational disadvantages. This type of approach has been used to control organic species (primarily taste- and odor-producing) for over 100 years, so the design procedures for filter hydraulics and backwashing are documented well in the literature. However, the Army design engineer should use caution in developing performance standards from standard design procedures. Instead, performance standards should be developed from isotherm data on the water and for the specific organic species of concern. The mean bed contact time should then be determined to calculate projected performance from the isotherm data.

For complex organic species, the filter cap approach to GAC treatment does not permit enough carbon contact time or process flexibility to meet requisite quality criteria.⁷⁴ In these cases, carbon columns or beds may provide an effective alternative that meets the contact time and operating flexibility requirements for the organic species of concern. These columns or beds can be in the form of a pressure contactor in a steel tank or a gravity contractor in an open concrete tank. Figure 11 shows both.⁷⁵

The pressure contactor may be the better choice for small groundwater systems because one pumping stage can be used to pass water through the filter and into the distribution system.⁷⁶ However, gravity beds also have an advantage because the

⁷¹J. C. Krulthof.

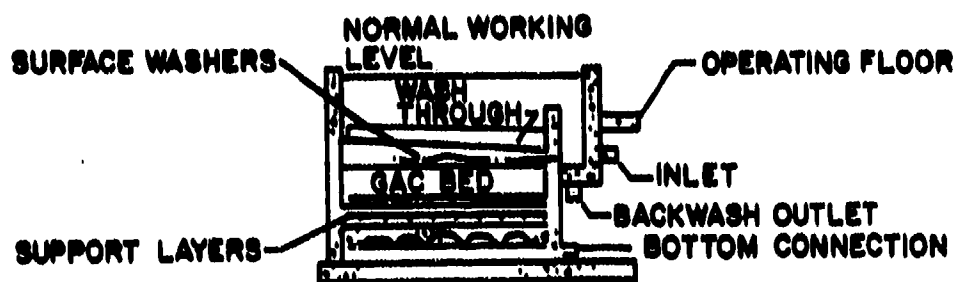
⁷²J. C. Krulthof.

⁷³S. P. Shelton, et al., *A Model for the Cost Effective Design of Water Treatment Unit Operations* (USEPA/MERL, February 1983).

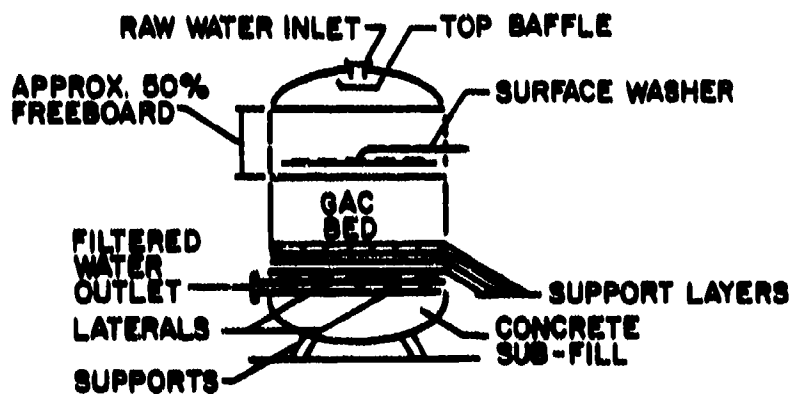
⁷⁴S. P. Shelton, et al., 1983.

⁷⁵V. Snoeyink.

⁷⁶V. Snoeyink.



GRAVITY CONTACTOR



PRESSURE CONTACTOR

Figure 11. Carbon contactors. (From: V. Snoeyink, "Control Strategy--Adsorption Techniques," *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water* [AWWA Research Foundation, 1983.] Used with permission.)

(1) concrete tank is not susceptible to corrosion and (2) the bed's condition can be viewed easily since it is open to the atmosphere.

A carbon column's flow rate and bed depth can be approximated from isotherm data. However, the operational cost of GAC column systems makes it prudent to perform pilot-scale investigations to define the most cost-effective flow and bed depth to meet the organic species removal criteria. These variables will be related to the rate of organic species adsorbance and environmental conditions such as pH and temperature. Typical column configurations for pilot testing have flow rates of 2 to 10 gpm/sq ft and carbon bed depths of 10 to 30 ft. In pilot-plant investigations, column diameters as low as 6 in. can be used without significant error due to wall effects.

The prospective carbon types should be evaluated using the isotherm tests described previously. The best one or two carbons may then be subjected to pilot-scale testing.⁷⁷ It is not necessary to run pilot tests on a large variety of carbon types; the pilot test's purpose is to refine design variables to:

1. Compare between the best two candidate carbons under the same dynamic flow conditions.
2. Determine the minimum required contact time to meet requisite organic species quality requirements.
3. Confirm manufacturers' data relative to bed hydraulics and head loss for various configurations.
4. Determine carbon dosage requirements, which subsequently will affect regeneration alternatives.
5. Evaluate the impact of various pretreatment alternatives on the carbon column performance, dosage, and cost if the treatment facility has not been predetermined.
6. Evaluate the columns' feasibility versus capped filters relative to rate, dosage, and other design variables.

In all pilot plant tests, care should be taken to duplicate the water that will be processed in the full-scale operation. Although pH and temperature are the two major components influencing performance, other properties of the water can also affect system performance.

The removal effectiveness for a specific organic compound may be influenced by the presence of other organic compounds that compete for adsorption sites on the carbon. For instance, the adsorptive capacity of dichlorophenol was reduced when a small amount of trichlorophenol was present in water to be treated.⁷⁸ Humic acids also have been found to interfere with adsorption by competing for adsorptive sites. For these reasons, removal efficiencies for a given compound may vary from one installation to the next or even within the same installation if raw water quality changes over time. Thus, it is advisable to use the water to be treated when testing candidate brands of activated carbon before purchasing.

⁷⁷ P. V. Roberts and R. S. Summers, "Performance of Granular Activated Carbon for Total Organic Carbon Removal," *JAWWA*, Vol 74, No. 2 (February 1982).

⁷⁸ V. Snoeyink.

Once pilot-plant data are developed, the column can be designed. Many factors influence the design of contactors for GAC systems, but one of the most important to consider is whether full advantage is taken of reserve adsorption capacity by using countercurrent upflow contactors. "Reserve capacity" refers to the carbon's ability to reduce an organic to some degree, but not enough to meet the requisite criteria. For example, if the requisite criteria for a particular organic species were 10 µg/L, the carbon, when considered to be exhausted, could no longer adsorb the organic from a solution containing 10 µg/L. However, the same carbon may still have the capacity to reduce the influent organic from 100 to 30 µg/L. This concept can be extrapolated until the carbon will not adsorb the organic at 100 µg/L or is totally exhausted and must be replaced or regenerated. By using an upflow countercurrent column in which fresh carbon is added to the top and spent carbon is removed from the bottom, all carbon in the system can be completely exhausted before replacement or regeneration. Full countercurrent operation can be obtained best in upflow beds because the spent carbon can be withdrawn easily from the column base (gravity) and the carbon particles tend to maintain their spatial integrity since carbon density increases as a function of the amount of organics adsorbed.

GAC Case Studies

GAC has been recognized as being able to effectively remove a broad spectrum of organic compounds, including chlorinated hydrocarbon solvents, pesticides, and THMs. Pilot GAC plants in the Netherlands measured 75 to 95 percent removal of p-dichlorobenzene.⁷⁹ Removal of other chlorinated hydrocarbons also was good. There are 50 GAC plants operating in the United States and seven of these are for removing specific organic compounds.⁸⁰

Two wells serving Woodbury, CT (total well capacity 0.15 MGD) became contaminated with TCE and several other volatile organic compounds. TCE concentrations were as high as 120 µg/L. An existing softening unit was retrofitted as a pressurized GAC system composed of three 60-cu ft downflow beds.⁸¹ TCE concentration was brought to below 25 µg/L and that of other organics to below detectable levels.

GAC was used to treat groundwater contaminated with TCE and ethers in Rockaway Township, NJ, where TCE levels were as high as 220 µg/L.⁸² Two downflow pressure GAC beds, each 10 ft in diameter and 20 ft high and containing 20,000 lb of 8 X 30 mesh GAC, were installed. TCE concentrations were reduced to acceptable levels, although the ethers exhausted the adsorptive capacity of the bed sooner than expected. This system's capital cost was \$200,000. Operating costs for this and other GAC systems used to remove chlorinated hydrocarbons ranged from \$0.08 to \$0.38 per thousand gallons.⁸³ The higher operating cost for Rockaway Township is due to the frequent replacement of carbon.

An example of design and operating parameters for a GAC plant is provided by a plant at Zevenbergen, Netherlands.⁸⁴ This plant has an average loading of 76,610 gal/hr

⁷⁹W. C. VanLier, et al.

⁸⁰J. C. Krulthof.

⁸¹V. Snoeyink.

⁸²V. Snoeyink.

⁸³V. Snoeyink.

⁸⁴J. C. Krulthof, et al., "Design, Construction and Operation of Carbon Filters," *Activated Carbon in Drinking Water Technology* (AWWA Research Foundation, 1983).

and was constructed to remove toxic organic compounds such as pesticides and insecticides and to improve taste. The actual plant design capacity is 211,338 gal/hr distributed over three open concrete filters, each 2048 cu ft. The bed depth is 6.9 ft, velocity is 11.1 ft/hr, and EBCT is 37 min. The plant's operation is completely automated. Carbon life is 1 to 2 years or about 20,000 to 25,000 bed volumes. The filters are equipped for backwashing, but this is not done during a normal filter run. The carbon is delivered in bulk by truck and is unloaded into the beds through a pipe. After filling to a uniform depth, the filter is backwashed several times to remove dust and ensure the carbon's uniformity. To remove the carbon for regeneration (every 1 or 2 years), it is pumped as a slurry (20 percent concentration) at a rate of about 440 gal/min. The objective is to minimize abrasion of the carbon. About 10 percent of the carbon is then lost during regeneration. The total capital cost (including engineering and construction) for the GAC plant was \$1.46 million (1983 dollars).

Estimating GAC Costs

Equations for estimating the annual capital and operating and maintenance (O&M) costs for GAC systems have been formulated. Costs for the contactor, carbon, and regeneration (transportations, storage, and regeneration) are calculated separately.⁴⁵ Capital cost equations for the contactors are done on a volume-per-individual contactor basis, and it is assumed that the unit is completely housed. The equations exclude equipment for surface washing and backwashing, the initial carbon charge, and carbon handling facilities outside the pipe gallery or building. O&M cost equations for contactors are on a square foot basis.

One option is to convert an existing sand filter to a GAC contactor and, therefore, a separate equation is included. With this option, carbon handling ducts would have to be installed.

Table 14 shows the design assumptions used in deriving the equations and Table 15 shows the equations. Other necessary equations are for initial carbon supply and replacement of carbon lost after regeneration:

$$\frac{\text{Carbon supply, \$ / yr} = (\text{lb GAC})(\text{cost, \$ / lb})}{\text{x (annual capital recovery factor)}} \quad [\text{Eq 4}]$$

$$\frac{\text{Carbon replacement, \$ / yr} = (\text{lb GAC replaced})}{\text{x (cost, \$ / lb)(No. replacements / yr)}} \quad [\text{Eq 5}]$$

It is assumed that carbon would be regenerated offsite at a multihearth facility. (Equations for estimating costs of regenerating the carbon onsite are found elsewhere.⁴⁶) The estimates require using two equations: one for transportation and storage, and one for regional multihearth regeneration. The latter equation should be multiplied by percentage use. The area given in the size range column for transportation, storage, and regeneration is in square feet of hearth area. The number of pounds per day of carbon to be regenerated should be divided by 70 lb/day-sq ft of hearth area to find hearth area to be used in the equation.

⁴⁵ R. M. Clark, et al.

⁴⁶ R. M. Clark, et al.

Table 14

Assumptions for GAC Cost Equations*

Design Parameters for Postfilter Adsorption	
Parameter (1)	Value (2)
Activated carbon cost	\$0.85/lb (\$1.43/kg)
Activated carbon loss per reactivation cycle	7%
Natural gas cost	\$0.0013/scf (\$3.679 x 10 ⁻³ /SM ³)
Electric power cost	\$0.04/kWh
Construction cost index	325.0
Producers price index	243.8
Direct hourly wage rate	\$11/hr
Amortization rate	8%
Amortization period	20 yr
Loss in adsorptive capacity	0%
Design capacity	70%
Empty bed contact time	18 min
Reactivation frequency	Every 2.4 months

Assumptions for Separate Postfiltration Systems

Item (1)	Design Capacity in MGD (m ³ /day)				
	1 (4,000) (2)	5 (20,000) (3)	10 (40,000) (4)	100 (400,000) (5)	150 (600,000) (6)
Number of contactors	3	6	12	40	60
Diameter of contactors, in ft (m)	8 (2.4)	12 (3.7)	12 (3.7)	20 (6.1)	20 (6.1)
Depth of contactors, in ft (m)	13 (4.0)	13 (4.0)	13 (4.0)	14 (4.3)	14 (4.3)
Volume of GAC per con- tactor, in cu ft (m ³)	653.1 (18.5)	1,489.5 (41.6)	1,489.5 (41.6)	4,396.0 (124.4)	4,396.0 (124.4)
Minimum empty bed contact time, in min	18	18	18	18	18

*From: Clark, R. M., "Optimizing GAC Systems," ASCE/EEDJ, Vol 109, No. 1 (ASCE, 1983). Used with permission.

Table 15
GAC Capital and O&M Cost Equipment*

Unit	Size Range**	Capital Costs**	Operating Costs**
Concrete gravity contactor	350-10,600 cu ft (140-28,000 sq ft)	470 USRT ^{0.38} CCI NO	100 USRT ^{0.76} PR ^{0.28} PPI ^{0.15} DHR ^{0.48}
Steel gravity contactor	6280-14,100 cu ft (41400-62800 sq ft)	5.6 USRT ^{0.85} CCI NO	6.2 USRT ^{0.9} PR ^{0.4} PPI ^{0.11} DHR ^{0.39}
Pressure carbon contactor	390-2260 cu ft (340-2200 sq ft)	376 USRT ^{0.38} CCI NO	200 USRT ^{0.78} PR ^{0.32} PPI ^{0.2} DHR ^{0.33}
Convert existing filter	370-70,000 sq ft	6.5 USRT ^{0.91} CCI NO	(none)
Regional GAC transportation & storage	1000-20,000 sq ft 30,000-3,000,000 lb/yr	0.88 USRT CCI	0.00018 USRT PPI ^{0.2} DHR ^{0.63}
Regional multihearth regeneration	27-1510 sq ft	60 USRT ^{0.44} CCI NO	

*From: R. M. Clark, "Optimizing GAC Systems," ASCE/EEED, Vol 109, No. 1 (ASCE, 1983). Used with permission.
 **Capital cost USRT is given first, O&M USRT is in parentheses. USRT = use rate; CCI = construction cost index/100; NO = number of units; PR = power cost, \$/kWh; PPI = producer price index/100; DHR = direct hourly wage rate, \$/hr.

Other GAC costs have been estimated.⁸⁷ Table 16 shows capital and operating costs associated with TCE removal for three size categories of population, from 500 to 50 µg/L and 500 to 5 µg/L. Figure 18 (Chapter 5) shows GAC treatment costs for removing different chlorinated hydrocarbons compared with aeration costs.

Powdered-Activated Carbon (PAC)

PAC systems have been used widely in water treatment plants to remove organic materials that cause taste and odor problems. This narrow application has been expanded in recent years to include removal of THMs, and may be expanded in the future to include treatment of other as yet undefined organic species.

Isotherm data should be developed for PAC systems application using the procedures discussed previously. These data should be determined for the raw water as well as for various levels of treated water that represent the candidate points of applications within the treatment plant. The application point should be selected to ensure that the carbon and water will be mixed adequately, enough contact time is provided as indicated by the isotherm evaluation, and the organic species are in a form amenable to adsorption as indicated from the isotherm data. Typical application points that have been used in water treatment plants include the raw water, rapid-mix basin, flocculators, sedimentation basins, conduits to the filters, and the filter tops.

PAC applications to raw water usually have been effective for classical taste and odor objectives and THM precursor removal.⁸⁸ The influent conduit provides a long contact time and good mixing, and adsorption can occur before THM precursors have reacted with chlorine. The basin may be equally effective if chlorine is added at a later point or if chlorine does not affect the organic species of concern. Application to the flocculators or sedimentation basins does not appear to be as effective except when color or high turbidity levels are present. PAC addition to the top of the filters gives a good final polish to the water when used in conjunction with previous application, but this method may not be adequate for total treatment due to limited contact time. In PAC system design, several application points usually are provided to maximize operational flexibility.

A note of caution relative to regeneration technologies for PAC systems: many classical references indicate that PAC is not a good choice for long-term application since the carbon cannot be regenerated cost-effectively. However, recent innovations in PAC regeneration systems and other evolving technologies are decreasing the significance of that problem. For example, a new technique for using PAC has been pilot tested in West Germany.⁸⁹ The PAC is applied to a filter bed consisting of carrier material such as 1-to-3-mm styrene spheres. The bed is conditioned by recirculating water through it for 10 to 20 min to allow the PAC to adhere to the spheres. The bed is then operated as an upflow filter until breakthrough occurs. Then the PAC is washed from the carrier material and the resulting slurry is discarded. Dissolved organics removal was comparable to that using GAC plants. Advantages of this technique are that it has an easily adaptable PAC dosage with influent water quality, prevents

⁸⁷V. Snoeyink.

⁸⁸C. Oulman.

⁸⁹J. A. P. Meljers, et al., "The Use of Powdered Activated Carbon in Conventional and New Techniques," *Activated Carbon in Drinking Water Technology* (AWWA Research Foundation, 1983).

Table 16

**Preliminary GAC Costs for Controlling TCE in Drinking Water
(1981 Dollars x 1000)***

Removal of 500 µg/L to 50			
	System Size Category		
	100-499	1000-2499	10,000-24,999
Population served			
Capital expenditures	82.00	344.00	741.00
Cost per 1000 gal	1.53	0.9	0.22

Removal of 500 µg/L to 5			
	System Size Category		
	100-499	1000-2499	10,000-24,999
Population served			
Capital expenditures	82.00	344.00	741.00
Cost per 1000 gal	1.58	0.82	0.25

*From: V. Snoeyink, "Control Strategy--Adsorption Techniques," *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water* (AWWA Research Foundation, 1983). Used with permission.

desorption of already adsorbed compounds and biological growth on the carbon, and is amenable to automation. Further testing is needed to optimize the size of carrier material and contact time and to select the best brand of carbon before this method will find common use in water plants.

The USEPA has estimated the cost of treating water with various dosages of PAC. Table 17 lists these estimates for various sizes of treatment plants.

In summary, unit processes that use activated carbon adsorption to remove organic species probably are the most common organic treatment techniques. These processes have evolved over the past 100 years, first to control taste and odor in water supplies, then to remove refractory organics in advanced wastewater treatment and water reuse, and finally to control THMs and pesticides. Activated carbon treatment is anticipated to continue evolving as a primary treatment medium for organic species that become regulated in the future. This growth will be due to the method's flexibility and the relative wealth of alternative design approaches.

Table 17

Cost of Treating With Powdered Activated Carbon*

Plant Design Capacity m ³ /sec (MGD)	Powdered Activated Carbon Feed Capacity, mg/L**		
	5	15	30
0.438 (1)	2.84 (10.0)	3.09 (11.70)	3.19 (12.10)
0.219 (5)	0.85 (3.20)	1.24 (4.70)	1.29 (4.90)
0.438 (10)	0.61 (2.30)	1.30 (3.90)	1.06 (4.00)
0.657 (15)	0.55 (2.10)	0.95 (3.60)	0.98 (3.70)

*From: Culp/Wesner/Culp, *Evaluation of Treatment Techniques for Reducing Trihalomethanes in Drinking Water*, EPA Contract No. 68-01-8292 (July 1983).

**Average annual dosage is 5 mg/L for the 5-mg/L feed capacity, and is 10 mg/L for the 15- and 30-mg/L feed capacities. This is necessary because regulations restrict average annual dosage to an upper limit of 10 mg/L.

Ion Exchange and Synthetic Resins

Ion exchange is a process in which ions held by electrostatic forces to charged functional groups on the surface of a solid are exchanged for ions of similar charge in a solution in which the solid is immersed. Because the charged functional groups where exchange occurs are on the surface of the solid, and because the exchanging ions must undergo a phase transfer from solution to surface phase, ion exchange involves both adsorption and absorption in removing molecules from a fluid.

In unit process design, "ion exchange" typically refers to a contained bed of resin through which water is passed for treatment. "Resin treatment" is the process of feeding ion exchange or adsorption resin to the water at some point in the treatment process much like the PAC application discussed previously. When the resin and water become mixed, sorption occurs as the water moves through other unit operations. Once the sorption process is complete, the resin, like PAC, is recovered, regenerated, and reused.

Many different types of synthetic resins that differ both in matrix and functional groups have been used for adsorption. A few adsorbant types, such as the styrene-divinylbenzene and the phenol-formaldehyde resins, are made without additional functional groups. Typically, however, resins have functional groups that make it possible for substances to be taken up by ion exchange or by specific interaction with the functional group. The strong-base ion-exchange resins, for example, frequently have the quaternary ammonium functional group whereas the weak-base resins generally have an amine functional group. The strong-acid and weak-acid functional groups can remove substances from water by cation exchange; typical functional groups are the sulfonates and carboxyls. Furthermore, the degree of crosslinking between polymers constituting

the matrix can be varied and, thus, resins with different pore size distributions can be generated.

Several investigators in the United States and Europe have evaluated these resin types for potential application in removing organic species from potable water.⁹⁰ In general, they were comparable to activated carbons in removing organic species, with some notable variations. In some tests, the synthetic resins' capacity for removing trichloroethylene and other solvents was found to be two to three times that of GAC. In other cases, resins were less effective than GAC.⁹¹ Some resins have been successful for removing humic acids, others for low-molecular-weight organics, and still others for THMs. Resins generally are very selective for a specific compound of interest.

The two major deficiencies associated with synthetic resins are cost and regeneration problems. Specifically, these resins are considerably more expensive than activated carbon and often have much shorter cycle times. Furthermore, the cost and efficiency of resin regeneration is far less attractive than for activated carbon regeneration.

With current technology, resins are not applicable as a general organic adsorbent for potable water treatment. They are more selective than activated carbon and thus do not provide the broad range of organic species adsorption typically desired in potable water treatment. There are situations for which the resins could be superior to activated carbon when a single organic species is of concern; however, in these instances, information required on the specific resin-organic interactions would require pilot-plant investigations.

Removal of specific organic compounds using synthetic resins is an evolving technology. To date, no successful commercial applications of this technology have been reported for organic species control in potable water; however, the technology is improving and may eventually become both technically effective and economical.

⁹⁰C. T. Anderson and W. J. Main, "Trace Organics Removal by Anion Exchange Resins," JAWWA, Vol 71, No. 5 (May 1979); R. C. Dressman, et al.; E. G. Isacoff and J. A. Blittner, "Resin Adsorbent Takes on Chlororganics from Well Water," Water and Sewage Works Journal (W&SWJ) (August 1979); C. Oulman.

⁹¹O. T. Love and R. G. Ellers.

5 PHYSICAL TREATMENT/SEPARATION PROCESSES FOR CONTROLLING ORGANICS

Physical treatment/separation includes four groups that may apply to water supplies: evaporation/volatilization, distillation, stripping, and membrane processes. These methods remove both THMs and other trace organic compounds. Refer back to Table 9 to review the processes and the types and characteristics of compounds removed.

Evaporation/Volatilization

Evaporation/volatilization can be used to remove low-molecular-weight, volatile organics. It is unlikely that these species would be found in surface waters; however, in groundwater sources, compounds such as methane and other low-molecular-weight, volatile organics sometimes are present. When the groundwater is stored with a free surface, these compounds will escape to the atmosphere.⁹² If the organics are less volatile or concentrated such that they do not escape from the free surface, a forcing process such as air- or steam-stripping can be used.

Air-Stripping

Air-stripping is a mass-transfer operation that can reduce the concentration of medium to highly volatile, low- to medium-molecular-weight organics and dissolved gases.⁹³ Packed towers (Figure 12) are commonly used for air-stripping operations. The treated water is distributed evenly across the top packing surface and allowed to trickle down around the packing. Air is forced up (either by natural draft or blowers) through the packing material to create a countercurrent flow. The large surface area provided by the packing prolongs contact between the air and water. Organics and dissolved gases are transferred from the liquid to the gas phase because of the difference in concentration in each phase.

Compounds susceptible to removal by air-stripping include THMs, chlorinated benzenes, many simple halogenated organic compounds, some aromatic hydrocarbons, and some pesticides.⁹⁴ Probably the most attractive feature of air-stripping is that it can selectively remove many compounds that are poorly removed by activated carbon adsorption. Thus, air-stripping is a highly complementary process to activated carbon for waters containing high concentrations of a wide range of organic species. Furthermore, some of the same compounds that are not retained well by activated carbon attenuate well in the soil and are therefore common in contaminated groundwaters. Air-stripping offers a relatively inexpensive approach for removing many such organic species.

⁹²J. M. Symons and G. G. Robeck.

⁹³S. P. Shelton, 1982; J. E. Singley, et al., *Trace Organics Removal by Air Stripping* (AWWA Research Foundation, May 1980); J. E. Singley, et al., *Trace Organics Removal by Air Stripping*, Supplemental Report (AWWA Research Foundation, April 1981).

⁹⁴J. P. Mieure; J. E. Singley, et al., 1981.

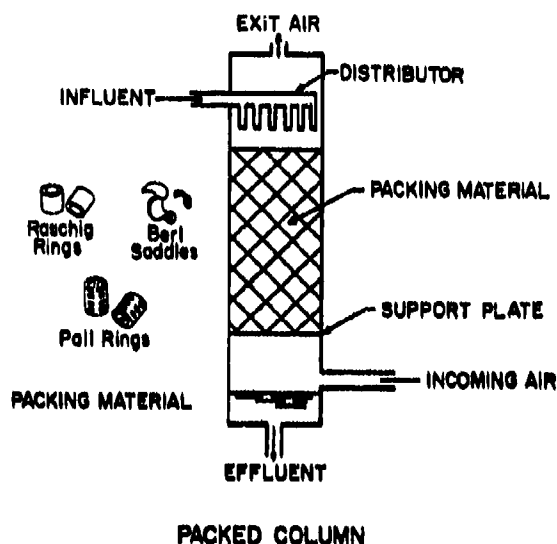


Figure 12. Packed tower aeration unit. (From: A. F. Hess, J. E. Dyksen, and H. J. Dunn, "Control Strategy--Aeration Treatment Technique," *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water* [AWWA Research Foundation, 1983.] Used with permission.)

Henry's Law and Equilibrium Models of Air-Stripping

Solubility and vapor pressure have long been recognized as important factors affecting air-stripping of organic materials. These factors are expressed in terms of Henry's Law which states that, under equilibrium conditions, there is a direct relationship between the concentration of a gas dissolved in a liquid and the partial pressure of the gas in air next to the liquid. In the case of organic compound removal, the organic contaminant would exist as a gas dissolved in the water to be treated and as a gas in the atmosphere. Henry's Law is expressed as:⁹⁵

$$P_g = H X_g \quad [\text{Eq 6}]$$

where P_g = partial pressure of the gas (atm)

H = Henry's constant (atm)

$$X_g = \frac{\text{moles of dissolved gas}}{(\text{moles dissolved gas}) + (\text{moles water})}$$

X_g is the fraction of moles of dissolved gas existing in equilibrium. Henry's constant, which Table 18 lists for several compounds, determines the amount of compound that can exist in liquid and gas phases under certain conditions. Thus, compounds with a higher Henry's Law constant are removed more easily by air-stripping. Checking Henry's Law constant for a compound of interest gives an indication of how easy it will be to remove

⁹⁵ Metcalf and Eddy, *Wastewater Engineering Collection Treatment Disposal* (McGraw-1972).

Table 18

Henry's Law Constants for Selected Compounds*

Compound	Formula	Henry's Constant (atm)**
Vinyl chloride	CH_2CHCl	3.55×10^5
Oxygen	O_2	4.3×10^4
Nitrogen	N_2	8.6×10^4
Methane	CH_4	3.8×10^4
Ozone	O_3	3.9×10^3
Toxaphene***	$\text{C}_{10}\text{H}_{10}\text{Cl}_8^+$	3.5×10^3
Carbon dioxide	CO_2	1.61×10^3
Carbon tetrachloride***	CCl_4	1.29×10^3
Tetrachloroethylene***	C_2Cl_4	1.1×10^3
Trichloroethylene***	CHClCCl_2	5.5×10^2
Hydrogen sulfide	H_2S	5.15×10^2
Chloromethane***	CH_3Cl	4.8×10^2
1,1,1-Trichloroethane***	CCH_3Cl_3	4.0×10^2
1,2,4-Trimethylbenzene***	$\text{C}_6\text{H}_3(\text{CH}_3)_3$	3.53×10^2 (25°C)
Toluene***	$\text{C}_6\text{H}_5\text{CH}_3$	3.4×10^2 (25°C)
Benzene***	C_6H_6	2.4×10^2
1,4-Dichlorobenzene***	$\text{C}_6\text{H}_4\text{Cl}_2$	1.9×10^2
Chloroform***	CHCl_3	1.7×10^2
Bromodichloromethane	CHCl_2Br	1.18×10^2 (EPA, 1980)
1,2-Dichloroethane***	$\text{CH}_2\text{ClCH}_2\text{Cl}$	61
Dibromochloromethane	CHClBr_2	47 (EPA, 1981)
1,1,2-Trichloroethane***	$\text{CHCl}_2\text{CH}_2\text{Cl}$	43
Sulfur dioxide	SO_2	38
Bromoform***	CHBr_3	38
Ammonia	NH_3	0.76
Pentachlorophenol***	$\text{C}_6(\text{OH})\text{Cl}_5$	0.12
Dieldrin***	$\text{C}_{12}\text{H}_{10}\text{OCl}_6$	0.0094

*Adapted from: M.C. Kavanaugh and R. R. Trussell, JAWWA, Vol 72, No. 12 (AWWA, December 1980). Used with permission. Boldface indicates compounds being considered for regulation.

**Temperature 20° C except where noted otherwise.

***Computed from water solubility data and partial pressure of pure liquid at specified temperature.

+Synthetic; approximate chemical formula.

the compound by aeration. Although Henry's Law constants are not as accurate for predicting removal efficiencies of certain water-soluble compounds,⁹⁶ they may be used in feasibility studies.

Henry's Law constants are affected by temperature, so that, for most volatile hydrocarbon compounds, the constants increase by a factor of three with every 10°C rise in temperature.⁹⁷ Therefore, the removal efficiency may vary in locations with extreme temperatures.

A volatile organic compound's rate of mass transfer is expressed in terms of the effective surface area and the difference between the equilibrium concentration (in gas and liquid phases) and the concentration in the liquid:⁹⁸

$$M = K_L a (C_l^* - C_l) \quad [\text{Eq 7}]$$

M = Mass transfer per unit time and volume (lb/hr/cu ft)

K_L = Liquid mass transfer coefficient (ft/hr)

a = Effective area (sq ft/cu ft)

C_l^* = Liquid phase concentration in equilibrium with the gas phase concentration (lb/cu ft)

C_l = Liquid phase concentration (lb/cu ft).

The value of K_L depends on the nature of the compound being removed as well as on the aeration device's configuration, the temperature, and the flow rate through the unit.

Air-stripping can use either diffused aeration or waterfall. In diffused aeration, air is injected into the water to be treated (Figure 13). Gas transfer is improved by increasing the aeration basin depth, producing smaller bubbles, altering the basin geometry, or using a turbine to reduce bubble size.⁹⁹ Waterfall aeration is done with multiple tray aerators, cascade aerators, spray nozzles, or countercurrent packed columns. Figure 14 shows a redwood slat tray aerator.

A USEPA pilot study on diffused aeration used water spiked with TCE to concentrations ranging from 100 to 1000 µg/L.¹⁰⁰ With a contact time of 10 min and an air-to-water ratio of 4:1, 70 to 90 percent TCE was removed. Another pilot plant for TCE removal was operated in Glen Cove, NY.¹⁰¹ TCE concentration in the raw water ranged from 132 to 313 µg/L. Contact times and air-to-water ratios were varied from 5 to 20 min and from 5:1 to 20:1, respectively. Up to 73 percent removal was achieved. When the air-to-water ratio was increased to 30:1, up to 90 percent of the TCE was removed.

⁹⁶ A. F. Hess, J. E. Dyksen, and H. J. Dunn, "Control Strategy--Aeration Treatment Technique," *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water* (AWWA Research Foundation, 1983).

⁹⁷ A. F. Hess, J. E. Dyksen, and H. J. Dunn.

⁹⁸ A. F. Hess, J. E. Dyksen, and H. J. Dunn.

⁹⁹ AWWA, 1983.

¹⁰⁰ AWWA, 1983.

¹⁰¹ AWWA, 1983.

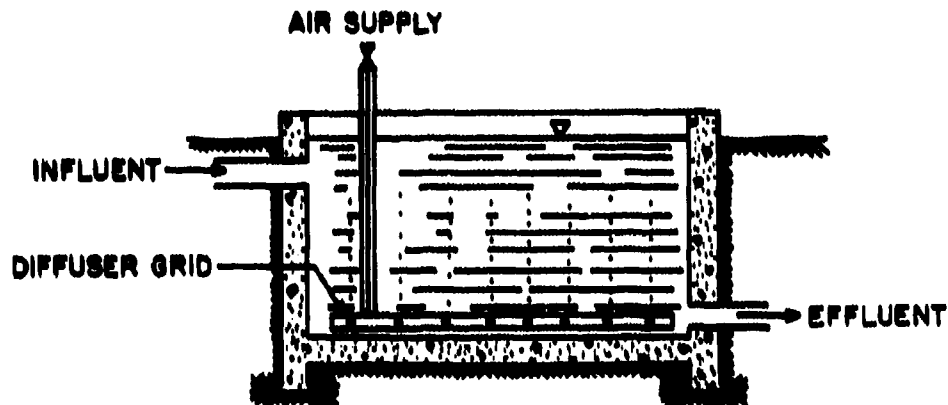


Figure 13. Diffused air basin. (From: A. F. Hess, J. E. Dyksen, and H. J. Dunn, "Control Strategy--Aeration Treatment Technique," *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water* [AWWA Research Foundation, 1983.] Used with permission.)

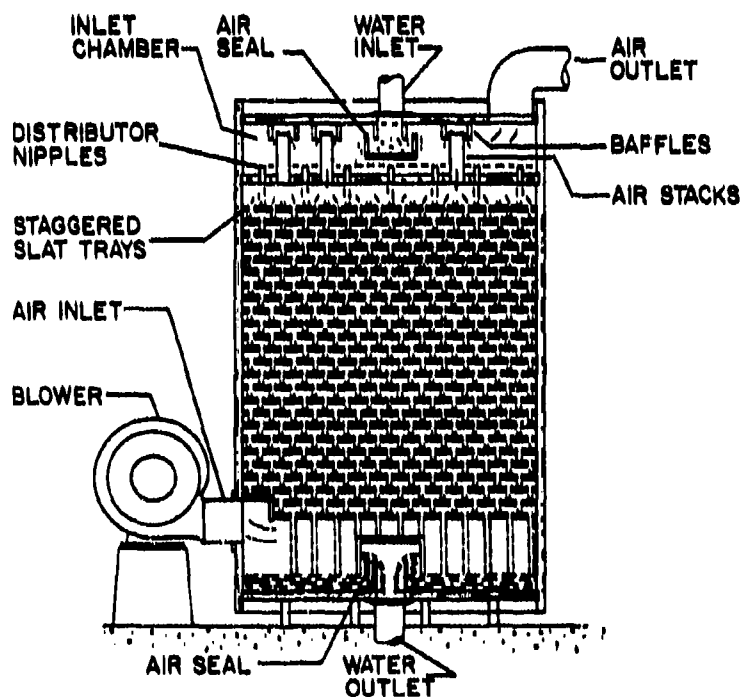


Figure 14. Slat tray aerator. (From: A. F. Hess, J. E. Dyksen, and H. J. Dunn, "Control Strategy--Aeration Treatment Technique," *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water* [AWWA Research Foundation, 1983.] Used with permission.)

Tray aerators often have been used to remove organic compounds from water supplies. One example is at Smyrna, DE, where two wells became contaminated with TCE in concentrations up to 72 $\mu\text{g/L}$. Water from one well was treated in a metallic tray aerator followed by GAC adsorption; water from the other well was treated in a redwood slat aerator followed by GAC. Even without the GAC, TCE removal was 40 to 60 percent, and after GAC treatment, 90 percent removal was obtained.¹⁰² The city of Norwalk, CT, also used tray aerators to obtain similar removal rates for TCE. Several other VOCs also were removed (75 percent removal for 1,1,1-trichloroethane and *trans*,1,2-dichloroethylene and 100 percent removal for 1,1-dichloroethylene).¹⁰³ The tower was 20 ft high and had a cross sectional area of 200 sq ft.

An example of using spray nozzles was for a 1 MGD private well water supply in West Palm Beach, FL. In 1980, several VOCs were detected, including TCE, vinyl chloride, 1,1-dichloroethylene and other chlorinated hydrocarbon solvents. Three 8000-sq ft spray ponds were constructed, each with 20 spray nozzles. Ninety percent of the dichloroethane has been removed and the operation has been working successfully.¹⁰⁴

A countercurrent packed column, another aeration technique, was applied in Rockaway Township, NJ (population 20,000). Half the population is served by wells, two of which became contaminated with TCE in concentrations varying from 50 to 220 $\mu\text{g/L}$; ether also was detected in the water. GAC adsorption was installed but the ether exhausted the carbon too soon. Then a countercurrent packed aeration column was installed to pretreat the water before it reached the GAC unit, and this system removed 95 to 99 percent of the ethers.¹⁰⁵ In addition, TCE was brought to below detectible levels. This removal rate requires high air-to-water ratios, as was seen in the previous examples of organics removal by aeration.

Full-scale stripping towers and decarbonators at Water Factory 21, Orange County Water District, CA, have shown a greater than 80 percent reduction in THMs, chlorinated benzenes, and halogenated ethanes. The stripping towers are natural draft whereas the decarbonators are small packed beds with forced countercurrent airflow. Good reductions of organic priority pollutants that have Henry's Law constants greater than $10^5 \text{ atm m}^3/\text{mole}$ were attained.

Concern has been raised that air-stripping may cause air pollution. However, measurements of volatile organics in air near the top of a pilot aeration plant were considerably less than the allowable occupational exposures. At this time, aeration is not viewed as a likely cause of air pollution by chlorinated hydrocarbon compounds.

Design Considerations and Costs—Aeration Units

The following factors should be considered in designing an air-stripping system:

- Number and nature of the organic compound(s) to be removed
- Air-to-water ratio
- Column depth

¹⁰² AWWA, 1983.

¹⁰³ AWWA, 1983.

¹⁰⁴ AWWA, 1983.

¹⁰⁵ AWWA, 1983.

- Available surface area
- Air and water temperature.

The nature and mixture of compounds to be removed will determine how practical it will be to use aeration. A contaminated water supply may contain several compounds, some of which may be removable by air-stripping, while others are not. More volatile compounds with higher Henry's Law constants would be removed effectively by aeration; Table 19 shows the removal efficiency expected for various compounds. The amount of compound to be removed also has bearing on the type of aeration unit to use. Figure 15 shows, for a range of Henry's Law constants, the aeration unit that could be expected to achieve various degrees of removal.¹⁰⁶ In general, for 90 percent removal or less, spray towers or diffused aeration units are more economical. If more than 90 percent removal is needed, a packed tower usually will be necessary.

The air-to-water ratio influences the removal efficiency and depends on the amount of air and water entering the unit. As seen in the examples presented in this chapter, a high air-to-water ratio sometimes is necessary to achieve the required degree of removal. With a 15-ft column filled with 1-in. size packing, 95 percent TCE can be removed using an air-to-water ratio of 20:1, but removing the same percentage of 1,2-dichloroethane requires an air-to-water ratio of 120:1.¹⁰⁷

The column depth will determine the unit's removal efficiency as well as capital cost. In pilot studies, the column depth can be varied while the air-to-water ratio is held constant. For example, with a 20:1 air-to-water ratio, 80 percent TCE can be removed with a 6-ft column; 99 percent removal requires a 10-ft column.¹⁰⁸ Figure 16 shows the relationship between packed column depth and air-to-water ratio typically needed to achieve 95 percent removal of three different organic compounds.

Available surface area determines the potential amount of compound that can be transferred from liquid to gas phase. For a packed tower aeration unit, this is a major consideration in designing the packing material configuration. One factor to keep in mind is that, in a packed column unit, the packing diameter should be about one-fifteenth the column diameter.¹⁰⁹

As previously stated, temperature influences Henry's Law constant, which in turn determines how much compound will exist in liquid or gas phase. Henry's Law constants increase as temperature rises.

In cost studies on aeration units, TCE removal usually is considered representative of average removal costs.¹¹⁰ Relative costs to remove the same amount of other organic compounds by aeration can be ranked in order of increasing removal costs:

1. Vinyl chloride
2. PCE

¹⁰⁶A. F. Hess, J. E. Dyksen, and H. J. Dunn.

¹⁰⁷A. F. Hess, J. E. Dyksen, and H. J. Dunn.

¹⁰⁸A. F. Hess, J. E. Dyksen, and H. J. Dunn.

¹⁰⁹A. F. Hess, J. E. Dyksen, and H. J. Dunn.

¹¹⁰A. F. Hess, J. E. Dyksen, and H. J. Dunn.

Table 19

**Percentage Removal of Organic Compounds Based on
Equilibrium Model as a Function of Henry's Law Constant**

V_A/V_W^*	Percentage Removal for Various Henry's Law Constants (H_1)			
	$H_1^{**} = 10^{-2}$	$H_1 = 3.4 \times 10^{-3}$	$H_1 = 10^{-3}$	$H_1 = 10^{-4}$
10	80	58	29	4
15	86	68	38	6
22	90	75	47	8
50	95	87	67	17
100	98	93	80	29

* V_A/V_W = the ratio of gas volume to liquid volume.
 ** H_1 is in atm m³/mole (to convert to atmospheres, multiply by 55,800).

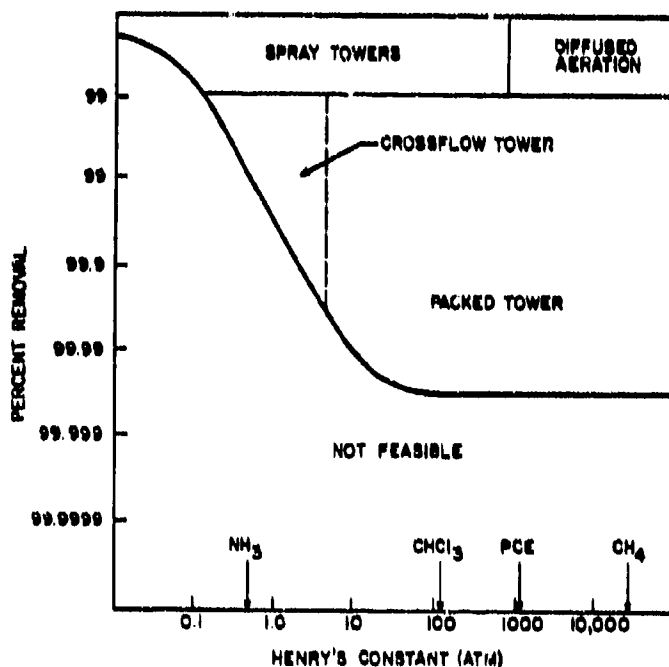


Figure 15. Removal efficiencies of various aeration devices. (From: A. F. Hess, J. E. Dyksen, and H. J. Dunn, "Control Strategy--Aeration Treatment Technique," *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water* [AWWA Research Foundation, 1983.] Used with permission.)

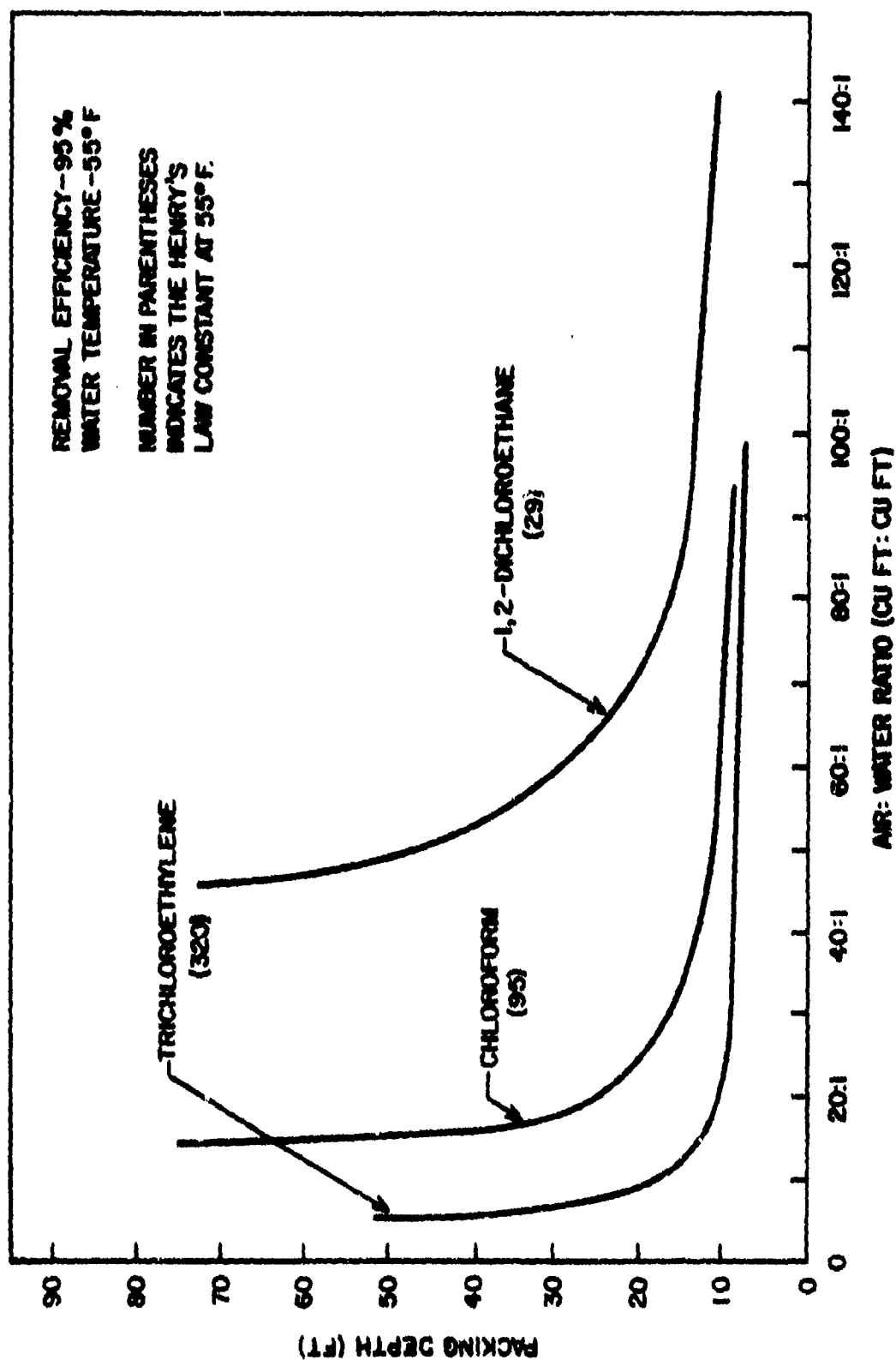


Figure 16. Packing depth vs air-to water ratios. (From: A. F. Hess, J. E. Dyksen, and H. J. Dunn, "Control Strategy--Aeration Treatment Technique," Occurrence and Removal of Volatile Organic Chemicals from Drinking Water ([A WWA Research Foundation, 1983.] Used with permission.)

3. TCE
4. Carbon tetrachloride
5. 1,1,1-Trichloroethane
6. 1,2-Dichloroethane.

The USEPA has formulated equations that can be used to calculate yearly capital and O&M costs for aeration units (Table 20).¹¹¹ The air-stripping cost equations consider both diffused aeration basins and aeration towers. Design constraints for diffused aeration basins include a rectangular basin design with a length-to-width ratio of 4:1, basin depth of 12 ft, maximum individual basin size of 3800 cu ft, air supply system sized for a minimum of 5 scfm/sq ft of basin floor area, minimum air-to-water ratio of 10:1, and continuous operation. For aeration tower design, constraints include a rectangular tower design with 16 ft of polyvinyl chloride (PVC) medium, overall tower height of 22 ft, and continuous operation.

The costs are annual, so capital and O&M costs must be added to obtain total treatment costs. The equations include factors for annualizing the capital costs over 20 years at 8 percent interest.

Approximate capital and O&M and total costs for plant sizes between 0.01 and 5 MGD can be estimated using the cost curves in Figures 17 and 18. These curves are for 90 percent removal of TCE, and Tables 21 and 22 list assumptions made in developing them.

Other costs can be approximated using the curves in Figure 19.¹¹² These curves show total treatment costs (1980 dollars) for both aeration and GAC for 90 to 95 percent removal of TCE, 1,1,1-trichloroethane, and carbon tetrachloride, demonstrating the wide range in costs for removing certain compounds. For example, to remove 1,1,1-trichloroethane, treatment costs increase little from 90 to 95 percent removal using tower aeration. However, if GAC treatment is used, the cost increases markedly (from \$0.04/1000 gal to \$4.00/gal for a 1-MGD plant) in increasing removal from 90 to 99 percent.

Thus, air-stripping may be an economical process for many contaminants of concern, particularly THMs and other halogenated methanes and ethanes. This process also can complement activated carbon adsorption, either by removing compounds that activated carbon will not treat or by extending the time between carbon regeneration cycles.

Steam-Stripping

Steam-stripping is a mass-transfer operation, similar to air-stripping, used to remove moderately volatile, medium-molecular-weight organic species.¹¹³ Steam-stripping can remove more organic species than air-stripping because the superheated

¹¹¹ P. Dorsey and R. M. Clark, *Drinking Water Cost Equations*, USEPA 600/2-82-055 (December 1982).

¹¹² O. T. Love and R. G. Ellers.

¹¹³ S. P. Shelton, et al., 1982.

Table 20

Capital and O&M Cost Equations—Aeration Units*

	Diffused Aeration	Aeration Tower
<u>Capital cost</u>		
size range (cu ft)	1900 to 380,000	640 to 256,000
Equation	$15.48 \text{ USRT}^{0.774} \text{ CCI}^{0.993}$	$11.59 \text{ USRT}^{0.7199} \text{ CCI}^{0.9985}$
<u>O&M cost</u>		
size range (cu ft)	1900 to 10,000	680 to 6400
Equation	$472.32 \text{ USRT}^{0.684} \text{ PR}^{0.553}$ $\text{PPI}^{0.0726} \text{ DHR}^{0.298}$	$31.36 \text{ USRT}^{0.625} \text{ PR}^{0.373}$ $\text{PPI}^{0.268} \text{ DHR}^{0.205}$
Size range (cu ft)	10,000 to 380,000	6400 to 256,000
Equation	$112.08 \text{ USRT}^{0.9247} \text{ PR}^{0.720}$ $\text{DHR}^{0.205}$	$6.54 \text{ USRT}^{0.946} \text{ PR}^{0.654}$ $\text{PPI}^{0.176} \text{ DHR}^{0.092}$

*USRT = Unit size, cu ft.

CCI = Construction cost index divided by 100.

PR = Power cost, \$/kWh.

PPI = Producer price index divided by 100.

DHR = Hourly wage rate, \$/hr.

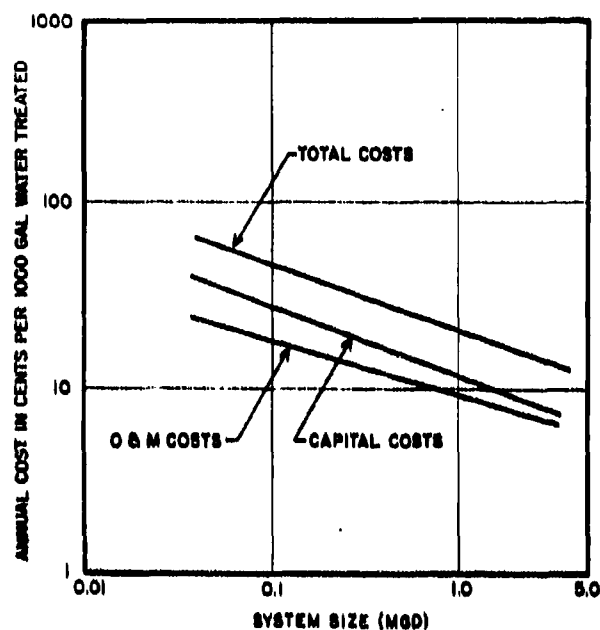


Figure 17. Cost curves for diffused aeration unit. (From: A. F. Hess, J. E. Dyksen, and H. J. Dunn, "Control Strategy--Aeration Treatment Technique," *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water* [AWWA Research Foundation, 1983.] Used with permission.)

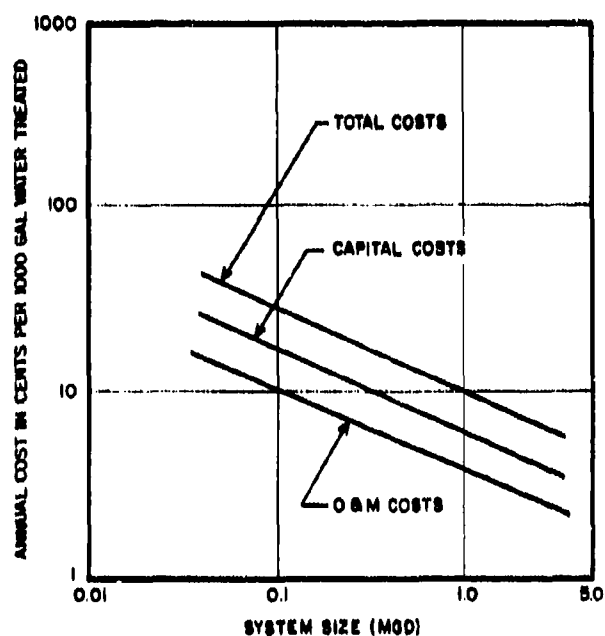


Figure 18. Cost curves for packed column aeration unit. (From: A. F. Hess, J. E. Dyksen, and H. J. Dunn, "Control Strategy--Aeration Treatment Technique," *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water* [AWWA Research Foundation, 1983.] Used with permission.)

Table 21
General Basis for Preliminary Cost Estimates
(1981 Dollars)*

Criteria	Assumptions
Removals	90% of TCE.
Capital costs	Capital costs are based on average plant capacities. All capital costs include costs for equipment or materials, installation, and contractor's overhead and profit.
Pilot studies	Were assumed to be required prior to selection and design of facilities, and costs for these are included in engineering.
Engineering, financial, and legal fees	15% of total construction cost.
Contingencies	15 % of total construction cost.
Operation and maintenance costs	All O&M costs were developed based on average daily plant production. Costs were based on cost curves in Culp/Wesner/Culp, 1979, and on estimates by Malcolm Pirnie, Inc., 1981.
Electrical charges	\$0.045/kWh.
Annualized capital cost	Total capital cost amortized over 20 years at a 10% interest rate.

*From: A. F. Hess, J. E. Dyksen, and H. J. Dunn, "Control Strategy--Aeration Treatment Technique," *Occurrence and Removal of Volatile Organic Chemicals from Drinking Water* (AWWA Research Foundation, 1983), pp 145-6. Used with permission.

Table 22

**Basis for Preliminary Cost Estimates—Packed
Tower Design (1981 Dollars)**

Criteria	Assumptions
<u>Diffused aeration design</u>	
Basins	Costs were developed from cost curves in Culp/Wesner/Culp, 1979, for 10% average plant capacity storage, modified to include diffused aeration.
Aeration equipment	Includes compressors for air supply and porous air diffusers for air introduction. Costs were based on information supplied by manufacturers.
Repumping	Includes pumps for repumping aerated water. Costs were developed from cost curves in Culp/Wesner/Culp, 1979, for in-plant pumping.
<u>Packed column design</u>	
Packed towers	Based on use of 1-in. packing. Most costs were obtained from Singley, et al., 1980. For the small system sizes not included in this reference, costs were based on information obtained from manufacturers. In addition to shells and packing, costs include tower internal parts such as mist eliminators flow distributors and redistributors packing supports, piping, and a clearwell under the tower.
Aeration equipment	Includes cost for blowers and air supply piping. Based on cost estimates in Singley, et al., 1980, and the Richardson Rapid Construction Cost, Estimating System.
Repumping	Includes vertical turbine pumps for supplying water to each stage of towers. Pump size was based on average plant capacity. Costs were on cost curves in Culp/Wesner/Culp, 1979, for in-plant pumping.
Housing	Includes a building to house the towers for cold weather protection, if necessary. Costs were based on \$2.00/cu ft of building.

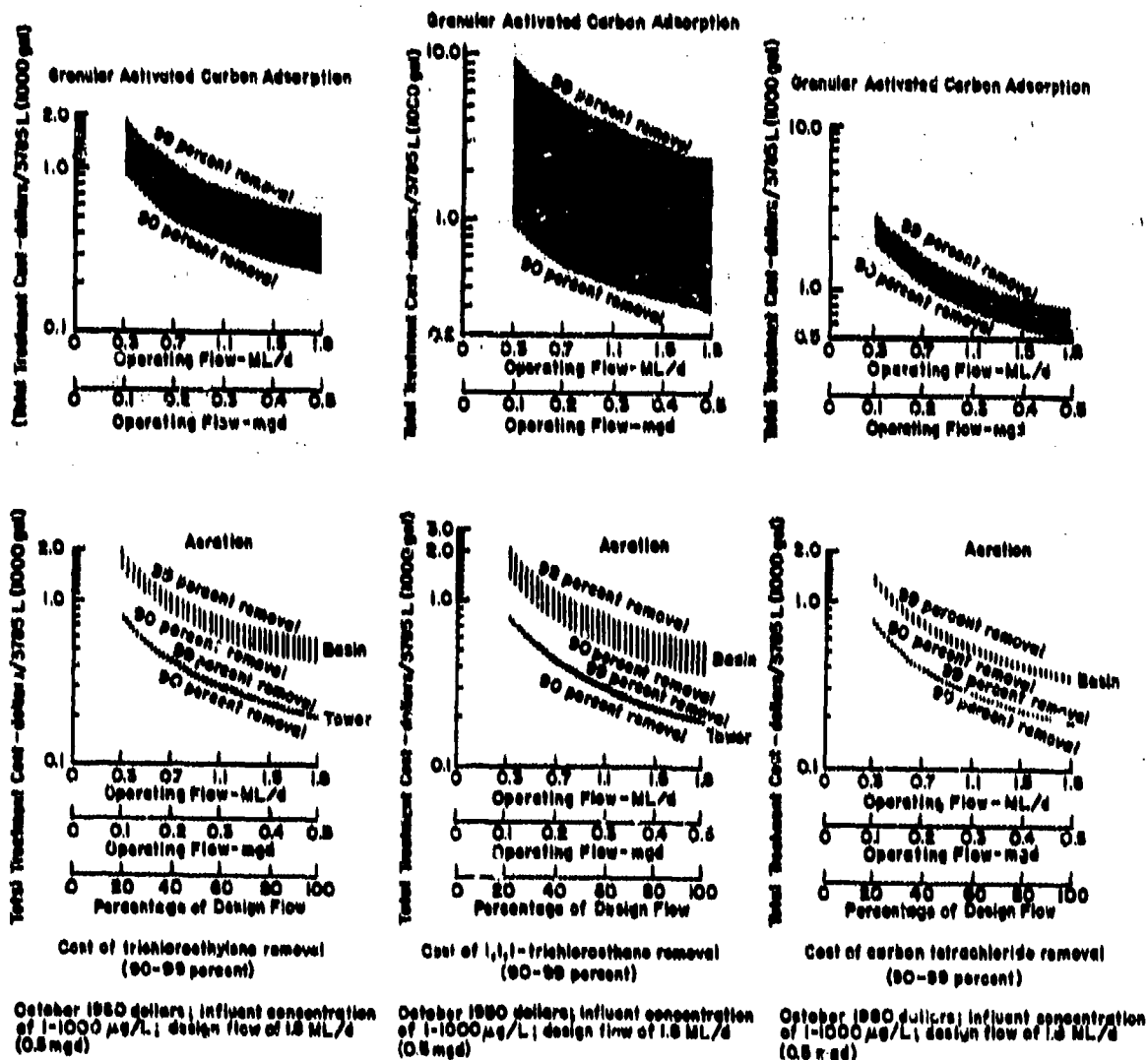


Figure 19. Cost curves for three chlorinated hydrocarbons. (From: O. T. Love and R. G. Ellers, "Treatment of Drinking Water Containing Trichloroethylene and Related Industrial Solvents," JAWWA, Vol 74, No. 8 [AWWA, August 1982]. Used with permission.)

steam alters equilibrium relationships favorably in terms of mass transfer from the liquid to the gas phase.

Sieve-tray stripping columns with relatively large still pots have been used widely by industry for organic product recovery and wastewater treatment.¹¹⁴ These systems treat anything from raw industrial slurries, fed directly to the still pot at the column base, to highly treated streams fed to up-tower trays for improved organic product recovery. As steam bubbles through the trays, the volatile organic species are stripped from the liquid fraction and routed to a condenser for recovery. Heavier components are withdrawn from the still pot. Steam-stripping systems have been designed to remove heavy compounds as still-pot residue while collecting water in up-tower trays and subsequently stripping volatile organics from the collected water.

At present, no steam-stripping operations are used for producing potable water.¹¹⁵ This discussion is included only because of the possibility that future organics criteria may become so stringent that systems with this level of sophistication will be required to produce a water of acceptable quality.

Distillation

Fractional distillation can separate constituents of a liquid mixture because of the constituents' differences in vapor pressure. This principle can be used to remove volatile species or to retain involatile ones. A distillation column designed and operated properly can yield nearly complete separation of water and both organic and inorganic species from the original mixture.¹¹⁶

Although a form of distillation has long been used for desalinating special-purpose water supplies, including naval onship systems or onshore facilities such as Guantanamo Bay, Cuba, and the Naval Arctic Research Laboratory at Point Barrow, AK, continuous countercurrent distillation columns have not been used to remove organic species from potable water supplies. This process does, however, offer excellent potential for producing high-quality potable water from a poor-quality source water which is heavily contaminated with all types of organic and inorganic species.

In this type of distillation, a water containing solids and/or heavy organics would be fed directly to the reboiler. As vapor rises through the column, it comes into continuous contact with a condensed portion of the vapor flowing countercurrently down the column along the trays. This process insures a vapor product enriched with volatile organic species. The liquid fraction of water recovered is then contacted countercurrently with a vapor stream from the reboiler in order to strip it of the volatile components (steam-stripping). The stripped liquid stream is the product water whereas the depleted heavy liquid in the reboiler is a waste stream.

Distillation like steam-stripping and solvent extraction, is a highly effective process for removing a broad spectrum of organic species from water. However, due to

¹¹⁴S. P. Shelton, et al., 1982.

¹¹⁵J. E. Dyksen and A. F. Hess III.

¹¹⁶S. P. Shelton, et al., 1982.

its high cost, this method has not found application as a unit process in current water supply practice.

Ultrafiltration

The most popular separation mechanism in ultrafiltration is selective sieving through pores.¹¹⁷ The ability of an ultrafiltration membrane to filter out (reject) a certain substance depends on the contaminant's molecular shape, size, and flexibility, as well as system operating conditions. A useful membrane must be able to separate distinctly at an economical rate, which means it must have a molecular weight cutoff and a high solvent flux at low-pressure differentials.

Ultrafiltration membranes generally have nominal molecular weight cutoffs for substances ranging from 500 to 1 million in molecular weight.¹¹⁸ The major application for ultrafiltration membranes is for removing colloidal material and large organic molecules from solution. For example, industrial applications have been successful in treating many process wastewaters. However, organics removal from prospective water supplies has received little attention, probably related to the fact that THMs and most other priority pollutants have molecular weights below 500; thus, ultrafiltration would not hold promise for removing these regulated contaminants.

Capital and operating costs for ultrafiltration units vary widely, depending on the application. Capital costs may be as low as \$0.50/gpd of installed capacity (whereas for industrial application it may be over \$5/gpd) and operating costs are about \$.22/1000 gal.¹¹⁹ If high-molecular-weight organic species become regulated to low levels in potable waters, ultrafiltration will be a potential unit process for controlling these contaminants.

Reverse Osmosis

Reverse osmosis separation is the combined result of (1) preferential solvent or solute adsorption at the membrane-solution interface and (2) interfacial fluid flow through the pores on the membrane surface.¹²⁰ Figure 20 shows this principle. The membrane's porous structure and surface chemistry together determine the solute and solvent flux through it. This flux is a function of the magnitude of preferential adsorption, the membrane's effective thickness, the size, number, and distribution of pores on the membrane surface, and the operating pressure, temperature, and flow conditions in the unit process.

The mechanism for inorganic rejection differs somewhat from that for organic rejection. Theories for reverse osmosis separation of inorganic ions in aqueous solution have been proposed on the basis of electrostatic repulsion of ions at the membrane-solution interface. Conversely, organic rejection is based on the polarity and sieve mechanisms determined by the organic molecule's size and shape. Certain types of

¹¹⁷W. A. Duvel, Jr., and T. Helfgott, "Removal of Wastewater Organics by Reverse Osmosis," *JWPCF*, Vol 47, No. 1 (January 1975).

¹¹⁸W. A. Duvel, Jr., and T. Helfgott.

¹¹⁹L. E. Applegate, "Membrane Separation Processes," *Chemical Engineering*, Vol 91, No. 12 (June 1984).

¹²⁰W. A. Duvel, Jr., and T. Helfgott.

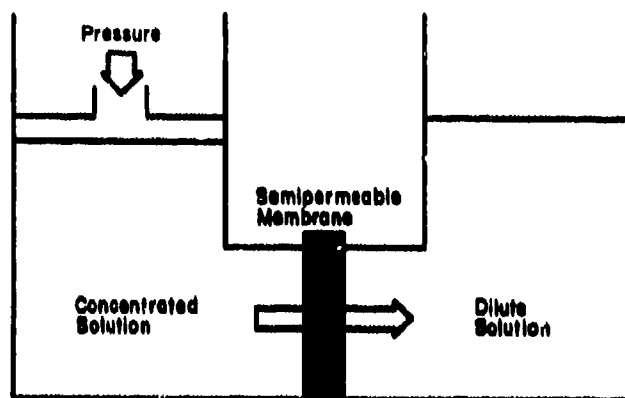


Figure 20. Principle of osmosis. (From: USEPA, *Treatability Manual*, Vol III, 3.1.16-2 [Office of Research and Development, September 1981].)

membranes reject better than others. Polyamide (aramid or nylon) membranes may have a smaller pore size than cellulose acetate membranes and can sieve better. Thin-film composite and aramid membranes also reject organics better than cellulose acetate membranes.¹²¹ The polar effect is more reluctant for cellulose acetate membranes and is determined by the acidity or basicity of the molecule concerned.

Organic rejections by several membrane types over a wide range of operating conditions are well documented in the literature.¹²² For example, a cellulose acetate membrane with an initial salt rejection of 97.3 percent, when subjected to seven different solutes on a series of short-run experiments, was modified such that the postexposure salt rejection was only 90.1 percent. Longer run data indicate that some organic solutes cause inherent membrane properties to change. During organic concentration, the membrane is exposed to several solutes for a relatively long period of time, and changes in the membrane's inherent rejection properties may result. One possible change is in the membrane's plasticization by adsorbed organic solutes that are not flushed out of the membrane.

Because most reverse osmosis applications have been for desalinization, capital and operating cost data are based on brackish and seawater plants. Reverse osmosis units designed for organics removal would be more comparable in cost to those treating brackish water. Table 23 shows typical capital and operating costs for reverse osmosis plants. In addition, capital and operating cost estimating equations for 1- to 200-MGD plants have been developed by the USEPA and appear in Table 24.

Application of reverse osmosis for removing organic species from potable water has not been widespread to date. However, reverse osmosis has good potential for removing some organic species, especially the priority pollutants and heavier organic molecules.

¹²¹ L. E. Applegate.

¹²² AWWA, "Controlling Organics in Drinking Water," *Seminar Proceedings*, AWWA Conference (AWWA Research Foundation, June 1979); W. A. Duvel, Jr., and T. Helfgott; M. J. McGuire, et al., "Assessment of Unit Processes for Removal of Trace Organic Compounds from Drinking Water," *JAWWA*, Vol 70 No. 10 (October 1978).

Table 23

Typical Costs for Reverse Osmosis*

Plant Type	Capital Costs (\$ per GPD)**	Operating Costs (\$ per 1000 gal)
<u>Brackish water plants</u>		
(Feedwater TDS 2000-5000 mg/L 80% conversion. Plant capacity 95%.)		
25 MGD	0.82	1.11
1 MGD	1.20	1.54
<u>Seawater plants</u>		
(Feedwater TDS 35,000 mg/L 30% conversion. Plant capacity 85%.)		
5 MGD	4.40	5.32
1 MGD	8.37	9.04

*From: L. E. Applegate, "Membrane Separation Processes," *Chemical Engineering*, Vol 91, No. 12 (McGraw-Hill, Inc., 1984), pp 76-77. Used with permission.

**All calculations assume a feedwater temperature of 21°C, minimum pretreatment, and no energy recovery. Operating costs would be reduced by 17% with energy recovery. Energy requirement is assumed to be 38 kWh/ 1000 gal.

Table 24

EPA Cost Equations for Reverse Osmosis Plants*

Assumptions

1. Feedwater total dissolved solids (TDS) concentration less than 10,000 mg/L.
2. Feedwater temperature 65 to 95°F.
3. Feedwater pH 5.5 to 6.0.
4. Brine disposal not included in cost estimate.
5. Single-pass system with an operating pressure of 400 to 450 psi.
6. Water recoveries:

<u>Flow range (MGD)</u>	<u>Water recovery (percent)</u>
1 - 10	80
10 - 100	85

7. Membrane life 3 years.

Capital cost = $40,564 (\text{plant size MGD})^{0.889} (\text{CCI})^{0.998} (\$/\text{yr})$.

O&M cost (\$/yr) = $602,393.12 (\text{plant size MGD})^{0.995}$

x (power cost \$/kWh) $^{0.4385} (\text{PPI})^{0.4570}$

CCI = Construction cost index/100

PPI = Producer price index/100

*From: *Drinking Water Cost Equations* (USEPA, December 1982).

6 FORMULATING AN ORGANICS REMOVAL STRATEGY

If unacceptable levels of organics are found in a water supply, an approach must be adopted for formulating a strategy to remove them. If THMs are of concern, Chapter 4 on alternative oxidants, moving the chlorination point, and activated carbon, and Chapter 5 on air-stripping should be consulted as well as USA-CERL Technical Report N-85/10.

The first step after finding that a water supply has been contaminated with organic compounds is to assess the magnitude of the problem. If the supply is groundwater, samples should be taken from other existing wells or new wells should be drilled for sampling. Try to determine the contamination source, because this will provide an indication of the area involved as well as the type of contaminants to look for in the analysis.

Site plans, topographic maps, aerial photos, and knowledge of the underlying geology also are useful. Talking to people familiar with previous activities (e.g., industry, dumping) in the area will help determine the contamination source as well as the type of organic compounds that may be present.

Wells should be sampled carefully by qualified personnel since sampling techniques can drastically affect results of the analysis. All samples should be fully analyzed by an EPA certified analytical laboratory; one well may have only one or two contaminants whereas another well in the same area may contain several compounds.

The quality of surface water supplies, especially rivers, tends to be more variable than that of groundwater. It may be that the contamination was temporary, with no contaminants found in the raw water upon further sampling.

When the water analysis results are available, review what types of compounds are present. Are the compounds listed in Tables 1, 2, or 3? Are they known or suspected to be carcinogenic? Are there several types, for example, some volatile and some nonvolatile? If so, more than one type of treatment may be necessary to remove all contaminants. Other key items are the concentration levels and the total flow to be treated. If a small flow from a single well is involved, perhaps that well could be closed. The contaminant concentration also will determine what percentage removal is necessary, for example, only a small percentage or over 90 percent removal.

In reviewing the contaminants present, use the information in previous chapters of this report to determine which removal methods possibly could be used to treat the water. For example, for volatile compounds, consider air-stripping; consider GAC for polar compounds. If the supply already is being treated, consider how the existing treatment processes could be enhanced to remove organics (particularly higher molecular weight compounds and THMs). Consider a combination of treatment techniques, particularly if the water contains more than one type of compound. For example, if heavier organics can be removed by improving coagulation/sedimentation, GAC could be used to treat remaining compounds that are sorbable. This series approach would provide more effective treatment as well as relieve the loading on the GAC bed. Figure 21 is a sample flowchart using a combination of methods. Treatment plus blending with an uncontaminated source could also be considered. Table 25 shows relative efficiencies of four treatment techniques for six chlorinated hydrocarbons, based on pilot-plant tests. If the contamination level is so high that treatment costs are prohibitive, the only workable alternative may be to find another potable water source.

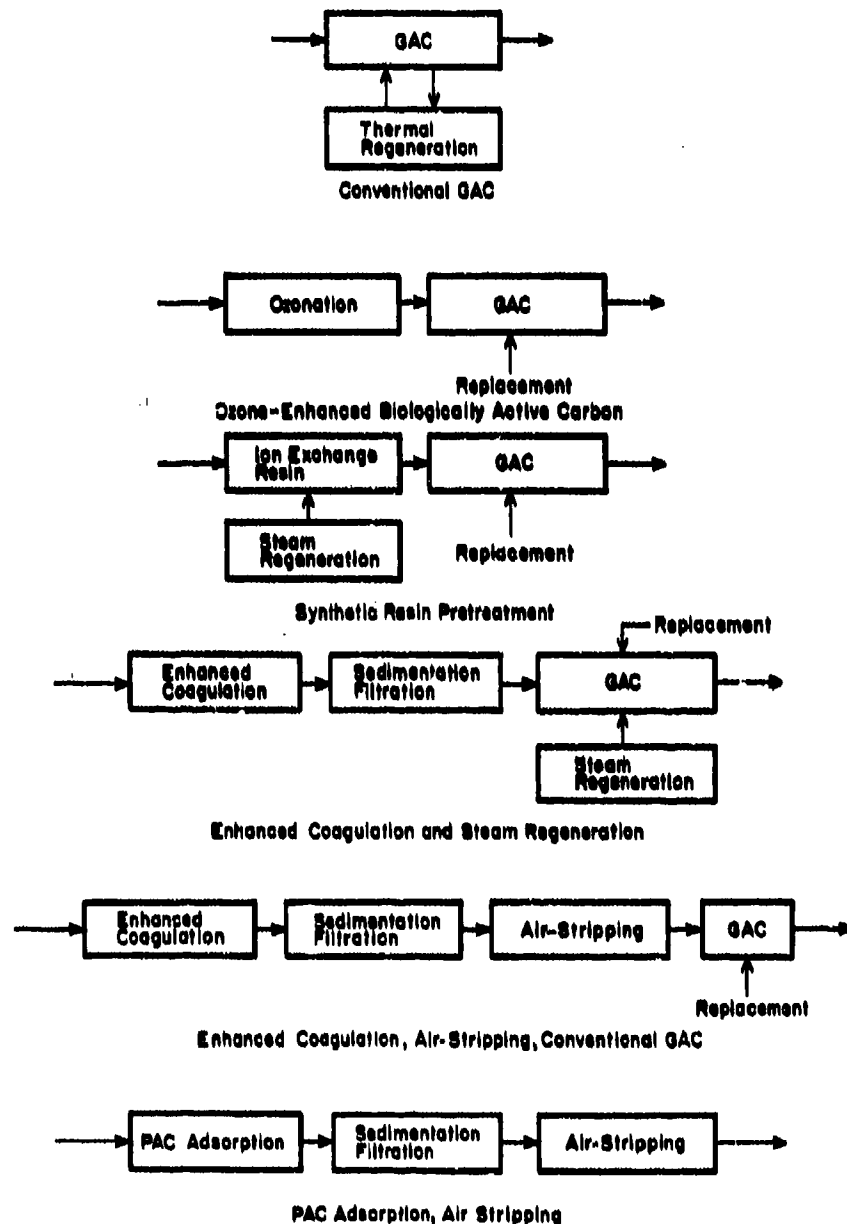


Figure 21. Parallel approach to organics removal. (From: R. R. Trussell and A. R. Trussell, "Evaluation and Treatment of Synthetic Organics in Drinking Water Supplies," JAWWA, Vol 72, No. 8 [AWWA, August 1980]. Used with permission.)

Table 25

**Relative Effectiveness of Treatment for Removing
TCE and Related Solvents (Based on Pilot Plant Tests)***

Solvent	Aeration	GAC Adsorption	Synthetic Resin Adsorption	Boiling
Trichloroethylene	2	1	1	5
Tetrachloroethylene	1	2	2	1
1,1,1-Trichloroethane	5	5	5	4
Carbon tetrachloride	3	3	6	3
<u>Cis</u> ,1,2-dichloroethylene	4	6	4	2
1,2-Dichloroethane	6	4	3	-

*Based on O. T. Love and R. G. Eilers, "Treatment of Drinking Water Containing Trichloroethylene and Related Industrial Solvents," JAWWA, Vol 74, No. 8 (AWWA, August 1982). Used with permission.

Costs for the proposed treatment techniques can be estimated based on the equations in Chapters 4 and 5. Capital and O&M costs usually are estimated on a dollars per 1000 gallon basis. Since more operating experience is documented with GAC and aeration plants, cost estimates are easier to make for these treatments. Equations for each are included so that, based on the units' size, capital and O&M costs can be compared. Cost curves and examples of treatment costs for various percentage removals also are included in Chapters 4 and 5. Based on cost estimates, a few preferred alternatives may be chosen. For newer treatment techniques such as ultrafiltration or synthetic resins, it may be necessary to consult equipment vendors for feasibility and cost information.

After preferred alternatives have been chosen, bench or pilot tests can be done, depending on the treatment. Bench testing is suitable for improving coagulation/sedimentation because jar tests can be done easily. GAC adsorption columns can be used in bench tests, whereas aeration units are more amenable to pilot-scale evaluation. If enough resources are available, more than one treatment technique can be tested and the results compared.

7 CONCLUSIONS

This study has provided fixed Army installations with information on sources, types, characteristics, and significance of trace organic compounds that may be found in drinking water; existing and proposed drinking water standards for trace organics; analytical techniques for measuring organic contaminants; and treatment processes and operational changes that could be made to conventional water treatment plants to control or remove organic contaminants from potable water. New and proven technologies for removing volatile trace organic compounds have been described and compared, with case studies and costs presented when available. Guidance has been provided for designing and selecting water treatment operational changes and trace organics removal equipment so that the most suitable, cost-effective strategy can be formulated for providing safe potable water.

Specific conclusions about mitigating organic species in water supplies include:

1. The future will bring improvements in techniques for identifying and quantifying organics in water supplies. With this progress, methods for defining high-molecular-weight organics that constitute the majority of the total organic carbon will be refined. Organic analysis apparently is progressing quickly from its present microgram-per-liter sensitivity to the picogram-per-liter level. This advance will greatly expand the number of organics of concern in drinking water supplies.

2. Unit processes for removing or destroying organics in a source water vary as a function of the organics' types, species, and concentration. Thus, as with analytical techniques for evaluating them, organics are removed or destroyed in water treatment unit operations using the organics' inherent polarity, volatility, and molecular weight characteristics.

3. The applicability of coagulants and alternative oxidants and disinfectant strategies in removing trihalomethanes (THMs) and other haloform precursors has been widened. It is possible that, with proper pH control, classic aluminum and iron salt coagulants can remove substantial amounts of raw organics that would otherwise form halogenated organics upon chlorination.

4. Unit processes that use activated carbon adsorption to remove organic species probably are the most widely used treatments. These processes have evolved over the past 100 years--first for controlling taste and odors in water supplies, then to control refractory organics in advanced wastewater treatment and water reuse systems, and finally to remove THMs and pesticides from water supplies. Activated carbon treatment probably will continue to evolve as one of the primary treatment media for organic species that become regulated in the future due to this medium's flexibility and the relative wealth of alternative design approaches.

5. Air-stripping may be an economical process for removing many contaminants of concern, particularly THMs and other halogenated methanes; or, it could complement the activated carbon adsorption process removing either compounds not amenable to activated carbon treatment or extending the time between carbon regeneration cycles.

6. Application of reverse osmosis for organic species removal from potable water supply has not been widespread to date. However, the literature indicates that the process has good potential for removing some organic species, especially the priority pollutants and heavier organic molecules.

7. If high-molecular-weight organic species become regulated to low levels in potable waters, ultrafiltration probably will be studied as a unit process for controlling these contaminants.

8. Solvent extraction, ion exchange, sorption resins, steam-stripping, and distillation are not feasible unit processes for treating water supplies under the current economic/regulatory framework. In the future, as technologies evolve and regulations become more stringent, these processes and others may have to be considered for use in order to meet organic contaminant criteria.

METRIC CONVERSIONS

$$1 \text{ in.} = 2.54 \text{ cm}$$

$$1 \text{ ft} = .305 \text{ m}$$

$$1 \text{ lb} = .453 \text{ kg}$$

$$1 \text{ oz} = 28.35 \text{ g}$$

$$1 \text{ gal} = 3.78 \text{ L}$$

$$1 \text{ sq ft} = .093 \text{ m}^2$$

$$1 \text{ cu ft} = .028 \text{ m}^3$$

$$1 \text{ psi} = 6.89 \text{ kPa}$$

$$^{\circ}\text{F} = (^{\circ}\text{C} \times 9/5) + 32$$

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